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# Canadian Journal of Research

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NUMBER 1

## THE CALIBRATION OF PLATINUM THERMOMETERS AT THE BOILING POINT OF SULPHUR<sup>1</sup>

By C. D. NIVEN<sup>2</sup>

### Abstract

A description is given of the means by which certain difficulties in experimental technique can be overcome. The construction and starting up of the apparatus in such a way as to avoid breakage of the boiling tube is described, and also the making and suspension of the radiation shield, and the general operation of the apparatus. The calculation of the resistance at 444.6° C. is discussed. Geometrical proofs are given for the relations from which the resistance at 100 and 444.6° C. are calculated, and special emphasis is laid upon the difference between the two formulas. The effect of errors in readings on the evaluation of  $\delta$  have been computed for a 10 ohm and a 32 ohm thermometer, and are shown diagrammatically. It is pointed out that errors in measurements of resistance at the steam point and the ice point are of far greater importance than errors in the measurements at the boiling point of sulphur. The conclusion is reached that with the present equipment one must not look for accuracy beyond the third decimal place in the value of  $\delta$ .

### 1. Introduction

According to the standard adopted by the International Committee on Weights and Measures, any temperature,  $t$ , on the temperature scale between 0° and 660° C., can be determined by measuring the resistance at that temperature of a platinum wire which conforms to a certain standard of purity, and by solving a quadratic equation in  $t$  of the form  $R_t = R_0(1 + At + Bt^2)$ .  $R_t$  is the resistance of the wire at the unknown temperature  $t$ , and  $R_0$  is its resistance at the melting point of ice, while  $A$  and  $B$  are two constants which are determined by measuring the resistance of the wire at two other known temperatures; for these two other fixed temperatures the boiling point of water and that of sulphur have been chosen.

The determination of the resistance at the melting point of ice and at the boiling point of water are comparatively simple procedures, but the determination at the boiling point of sulphur is not easy except for experienced workers. There are certain difficulties in working with a substance like sulphur; it is chemically reactive and ignites extremely easily; furthermore it solidifies when cool, so that in order to avoid breaking the boiling tube special precautions must be taken in starting up the apparatus. Again, a shield to prevent loss of heat from the thermometer by radiation has to be provided and suitably suspended. Such experimental difficulties taken singly may

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seem of little importance, but collectively they make the determination of the sulphur boiling point decidedly awkward. The literature avoids mention of some of these difficulties, and thus much time can be wasted quite unnecessarily in preliminary experiments by one who attempts for the first time to calibrate at the temperature of boiling sulphur. Therefore, in this paper there is described in detail a method of procedure which has been found to be comparatively simple. It is not implied that either the apparatus or the methods herein described are better than those which some other experimenter may have adopted; their employment should be looked upon, rather, as one satisfactory solution of a problem in experimental technique.

In addition to describing apparatus suitable for the calibration at the boiling point of sulphur, a few remarks have been added regarding the calculation of the resistance at the boiling point of sulphur under a pressure of 760 mm. of mercury, and also regarding the effect on the value of  $\delta$  of errors in the various readings necessary for its computation.

## 2. Apparatus

The general apparatus that was used for this work was built according to specifications laid down by Mueller and Burgess (3). Electricity was used for heating the boiling tube. A little difficulty was encountered in obtaining the porcelain tube upon which to wind the heater wire; this had to be specially supplied by a manufacturer. The turns of nichrome wire were held in place by coating the tube with alundum cement after winding. The heater tube thus constructed was placed inside a sheet iron cylinder, and rock wool was packed around it. The sheet iron cylinder was supported at the bottom of a heavy retort stand. Above this cylinder there was another somewhat similar one of the same diameter ( $6\frac{1}{2}$  in.) but measuring 18.5 in. in length. The bottom of this cylinder was fitted with a piece of asbestos-transite board, and in the centre of this board a hole was cut, through which the lower end of the sulphur boiling tube could pass. The latter could thereby be held centrally in the iron cylinder. This cylinder was supported by the heavy retort stand exactly above the shorter one containing the heater. Around that portion of the boiling tube, which, when in place, extended through this upper cylinder, was rolled a piece of flexible asbestos sheet. This was tied with two pieces of wire to keep it in place. The tube was then put into the cylinder and lowered until its lower end rested on a pad of asbestos wool inside the porcelain cylinder. The upper end of the tube was held centrally in the cylinder and asbestos wool was packed around it. A disc of asbestos sheet was cut to cover the top, and a hole in this disc served to hold the asbestos sheet, rolled around the tube, snugly against the latter. These details, which may not appear of much importance, are so fully described because it was only after they had been worked out that the constant breakage of boiling tubes was prevented.

The asbestos sheet wound around the tube permits the latter being completely withdrawn from the apparatus without disturbing the insulation.

The boiling tube can then be taken to a fume cupboard where it can be carefully heated over a Bunsen flame. In doing this the tube should be held at an angle and revolved, while the flame is allowed to play about two inches above the level of the solidified sulphur. Gradually the tube can be moved so that the flame plays on the sulphur near its surface. Liquid is soon observed to gather, accompanied by a receding of the sulphur from the glass wall. A rather alarming cracking sound can often be heard during this operation, but it will be found that it is not the glass tube that has cracked. In actual practice it has been customary to heat the electrically heated porcelain tube while the sulphur was being melted in the way just described; and not until a red heat could be observed on looking down into the apparatus was the heating of the sulphur in the flame discontinued and the tube replaced inside the insulating cylinder. If this procedure be followed, there is not the slightest danger of breaking a boiling tube in starting up the apparatus.

A great advantage in being able to take out the boiling tube is that it is then possible to see the amount of sulphur which it contains. According to Mueller and Burgess the tube should enter the heater to a depth of about 7 cm., and the height of the surface of the sulphur above the top of the porcelain tube should be about 5 cm. Thus the depth of sulphur in the boiling tube should be about 12 cm.

When the sulphur has been melted, the apparatus must be left in operation until the upper portion of the tube and the surrounding insulation have warmed up. If ignition of the sulphur vapor is to be prevented when the thermometer is put into the boiling tube, it is advisable to insert the thermometer as soon as possible after the sulphur has been melted and the tube replaced in the apparatus. The temperature of the blue flame which can be seen when sulphur burns appears to be so near to the temperature of boiling sulphur that the introduction of air into the tube, which is almost unavoidable when the shield is around the thermometer, is sufficient to cause the sulphur vapor to ignite with a mild explosion if the temperature in the boiling tube is high. No harm is done by the explosion but the faint and comparatively agreeable smell of boiling sulphur is at once changed to the disagreeable one of the dangerous gas sulphur dioxide.

The insertion of the platinum thermometer presents no difficulties if a bracket supported on the heavy retort stand—as described by Mueller and Burgess—has been provided. This bracket has a rack and pinion for raising or lowering the platinum thermometer in the tube as desired. It is advisable that the thermometer hang vertically so that on being lowered into the tube it will not touch the wall. Considerable difficulties however lie in shielding the thermometer, and the surmounting of these may prove very expensive. For instance, if the shield should drop down into the boiling tube as a result of a faulty suspension arrangement, the glass tube will probably be broken by the fall and the boiling sulphur will instantly ignite inside the porcelain heating tube; or again, as happened during the writer's work, the shield may

stick to the solidified sulphur adhering to the thermometer, and the attempt to release it, unless great care be taken, may result in the breaking of the quartz sheath of a valuable standard.

It has been found that a satisfactory method of supporting the shield is to hang it from the bracket from which the platinum thermometer is suspended. The umbrella of the shield should not fit tightly against the glass sheath, so that after the calibration is completed the thermometer can be easily withdrawn before any of the sulphur on the shield has had time to solidify.

As the making of the shield itself gave considerable trouble, the method of procedure finally adopted will be described. The length and diameter of a shield are fixed by the dimensions of the rest of the apparatus. According to Mueller and Burgess, the cylindrical portion should be 4 cm. longer than the coil of platinum wire in the thermometer, and the diameter of the cylindrical portion should be 1.5 cm. greater than that of the thermometer sheath. The required shield had, therefore, to consist of a cylinder 6 in. long and 1.25 in. in internal diameter. As it is desirable to have the shield "true," so that the thermometer hangs as nearly as possible in the centre of it, it was found much simpler to turn a piece of iron pipe to the required diameter than to attempt

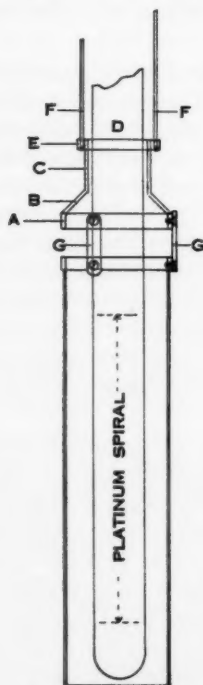


FIG. 1. Radiation shield which was found to be satisfactory and of simple design

to roll a piece of sheet iron. The wall of the shield could thus be made much thicker than would have been possible with a piece of rolled sheet, and the life of the shield was thereby increased. A lip of sufficient thickness to allow for the tapping of screwholes was left on one end of the cylinder when turning it down to the right diameter.

The work of Meissner (2)—subsequently verified by Mueller and Burgess—has shown that either iron or corrugated aluminium is satisfactory for use in the construction of the cylindrical portion of the shield. Meissner points out that the essential requirement is that the inside of the shield be a good "emitter" of black body radiation. Therefore aluminium cannot be used unless it be corrugated or in some other manner deprived of its metallic reflecting power. This detracts from its suitability as material for construction of a shield. Iron, on the other hand, is found to be very suitable so far as its radiation quality is concerned, but it corrodes very quickly in contact with sulphur vapor. It was, therefore, decided to make all parts of the shield, except the shielding cylinder itself, of aluminium. The umbrella was constructed from a piece of aluminium rod in the following manner. A rod of aluminium of diameter equal to that of the umbrella at the larger end was turned down so

that a short cylinder (A)—see Fig. 1—about  $\frac{1}{4}$  in. in length was left on the large end of the section of a cone (B) which formed the actual umbrella; a comparatively long cylinder (C) was left on the small end of this cone. The diameter of the cylinder on the small end of the cone was such as to allow the sheath (D) of the platinum thermometer to enter with ease, and on the end of the cylinder there was a lip (E) for attaching aluminium wires (F), employed to suspend the shield when placed inside the apparatus. The wall of the short cylinder (A) was left sufficiently thick to allow for the tapping of screw holes. Three holes were bored in it exactly opposite three other holes bored in the iron shielding cylinder, and by means of aluminium links (G) the umbrella and the shielding cylinder were held together. The umbrella was suspended with two aluminium wires hooked to two glass rods which, in turn, were hooked to two aluminium wires attached to the movable bracket supporting the thermometer. The glass rods were used as a precaution against heat losses, arising possibly from thermal conduction up the aluminium supporting wire. This type of shield is exceedingly simple to repair; when the iron portion has become badly corroded it is merely necessary to turn down a new cylinder to the correct size, and connect it by means of the three aluminium links to the uncorroded aluminium umbrella and supporting arrangement.

In the experimental procedure recommended by Mueller and Burgess, it is stated that the heating should be "so regulated that the condensation line is at least 1 cm. above the top of the insulating material." It has been found however that the condensation line, while fairly sharp itself, is considerably below the height to which evaporated sulphur can rise. The condensate of the sulphur vapor in the boiling tube can be observed when the preliminary heating over the Bunsen flame has lasted only for a short time and long before all the sulphur is melted. Furthermore, when the tube is replaced in the apparatus, sulphur particles can be observed rising out of the tube. In practice, two small pieces of aluminium plate have been used as a lid to prevent down draughts; these were not made to fit neatly, as it is essential that the pressure inside the tube be the same as that outside in the room. Around the edges of these small plates, where the sulphur vapor could pass, a floury yellow deposit could be observed when the apparatus was operating properly, long before the condensation line had reached the top of the tube. No further proof is, therefore, needed that sulphur vapor does escape into the room no matter how much care is taken to control the height of the condensation line, and for that reason alone, even if the objectionable accidents which result in the copious discharge of fumes of sulphur dioxide into the air never occurred, the boiling point apparatus should preferably be operated in an atmosphere that does not extend to the Wheatstone bridge or other measuring instrument. It might also be mentioned in this connection that it is very difficult to remove the thermometer from the boiling tube at the end of the calibration, without the sulphur, which may be dropping from it, catching fire and thus producing fumes of sulphur dioxide. The use of a fume cupboard is not as a rule feasible,



as the height required for the apparatus is about six feet, but since all lead resistance must be compensated for in any case, there is no reason why the boiling point apparatus should not be in a room separate from that containing the electrical measuring instruments—provided of course the barometer is in the former.

### 3. Measuring the Resistance of the Platinum Thermometer

If the barometric pressure remained constant during half an hour, so that readings could be repeated several times, there would be little trouble in calibrating a thermometer at the boiling point of sulphur. Unfortunately, however, barometric pressure varies very quickly and, indeed, remains absolutely constant only on rare occasions. On this account it is difficult to check readings on the Wheatstone bridge with a high degree of accuracy. The following method of taking readings was found to be satisfactory:—A pair of readings, which eliminated the lead resistance, was taken. The barometer was then read and another pair of readings was taken with the current reversed; the mean of these four readings was taken as the resistance measurement at that particular pressure. This seemed permissible, since reversing the current did not appear to affect the readings and was merely done as a precautionary measure. A set of readings taken in this manner was recorded two or three times and then the thermometer was raised in the boiling tube. No matter how high the line of condensation may be there is always a slight drop in the resistance of a shielded platinum thermometer when raised in the boiling tube. Peculiarly, however, with an unshielded thermocouple a lower temperature may be found near the surface of the

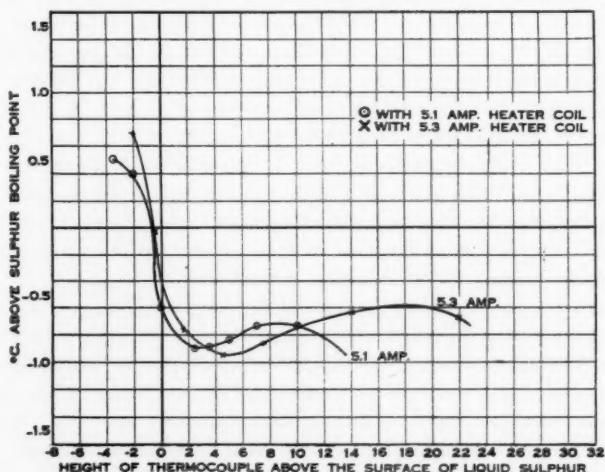


FIG. 2. Graph showing a very definite, though small, variation in temperature inside a boiling tube when the measuring instrument was a platinum-platinum-rhodium thermocouple, unprotected by a radiation shield.

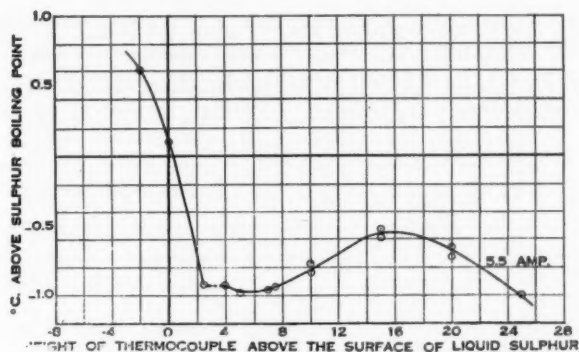


FIG. 3. Graph showing a very definite, though small, variation in temperature inside a boiling tube when the measuring instrument was a platinum-platinum-rhodium thermocouple, unprotected by a radiation shield, with 5.5 amp. in heater coil.

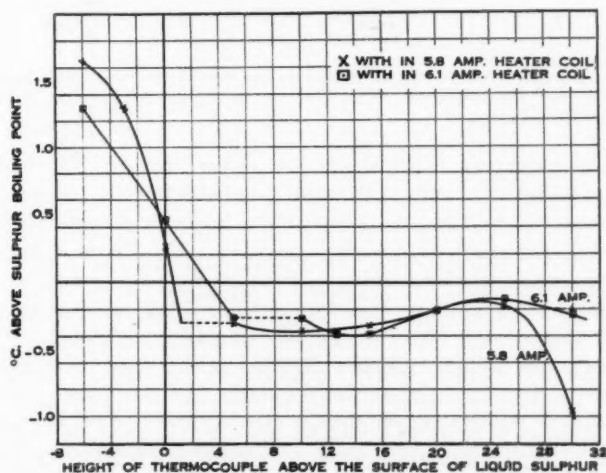


FIG. 4. Graph showing a very definite, though small, variation in temperature inside a boiling tube when the measuring instrument was a platinum-platinum-rhodium thermocouple, unprotected by a radiation shield.

sulphur than higher up in the tube. This experiment was done with a bare platinum-platinum-rhodium thermocouple and the phenomenon was observed repeatedly. In Figs. 2-4 typical curves are shown illustrating the variation of temperature in the tube with the height of the thermocouple. It can be seen that there is a minimum in each case. The various curves in Figs. 2-4 refer to the different amperages in the heating circuit, and if the height of the minimum be plotted against the amperage in the heating circuit, the points lie approximately on a straight line as shown in Fig. 5. The form of the curves is so unexpected that one would have been inclined to doubt the result, had not



Chappuis (1) also noted the same phenomenon. Chappuis did not consider the matter of much importance, as the effect disappears when the thermocouple is shielded—a fact which explains why those experimenters who used a radiation shield from the beginning of their work did not observe this

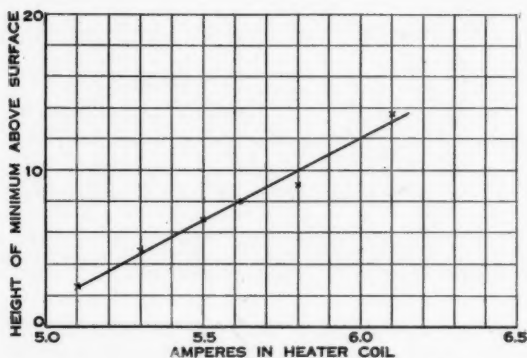


FIG. 5. Diagram showing a roughly linear relation between the height of the point of minimum temperature in the boiling tube, as found with an unshielded thermocouple, and the current in the heating coil.

lowering of temperature near the surface of the sulphur. Nevertheless the phenomenon is worth noting, since the experimenter who might hope to investigate carefully the conditions relating to equality of temperature inside the boiling tube, before actually calibrating with a shielded instrument, would be decidedly puzzled by his results.

It is hard even to suggest a cause for this unexpected phenomenon; possibly the sulphur vapor lower down in the tube is more transparent to radiation than the vapor higher up, and thus affords less shielding. Possibly a much more complex process may be at work, namely, the existence of two kinds of molecules with different temperatures of condensation; but, why the use of a shield should hide the phenomenon, if this be the explanation, is not clear.

#### 4. Calculation of the Resistance at 444.6° C.\*

In view of the fact that a small variation in atmospheric pressure causes a comparatively large change in the temperature at which sulphur boils, and therefore a comparatively large change in the resistance of the platinum thermometer immersed in the sulphur vapor, it is very useful to be able to calculate from each determination of resistance and pressure what the resistance at 444.6° C. should be, and thus ascertain how one's results are checking as the atmospheric pressure varies. In this calculation the formula which must be used is

$$R_{444.6} = R_s - \frac{R_{100} - R_s}{100} (t_s - 444.6) \times 0.882.$$

\* The author's thanks are due to Dr. Kaye, National Physical Laboratories, England, for some valuable assistance in this connection.

It is important to observe that this formula does not correspond exactly with the formula used to calculate the resistance at  $100^\circ \text{C.}$  from a steam point determination; if it did, one might expect in place of the multiplier  $\frac{R_{100} - R_0}{100}$ , either  $\frac{R_s - R_0}{t_s}$  or  $\frac{R_{444.6} - R_0}{t_{444.6}}$ , where  $R_s$  is the resistance in the sulphur vapor at the temperature  $t_s$ .

Since the derivation of the formulas whereby  $R_{444.6}$  and  $R_{100}$  are deduced from actual readings is not obvious, the following geometrical proofs are given in order to clarify matters.

Referring to Fig. 6, suppose the curve  $OCT$  relates the resistance,  $R$ , with the temperature,  $t$ , measured in degrees Centigrade. Draw ordinates at  $0^\circ \text{C.}$ , at  $100^\circ \text{C.}$ , and at  $(100 + \Delta t)^\circ \text{C.}$ , where  $100 + \Delta t$  represents the

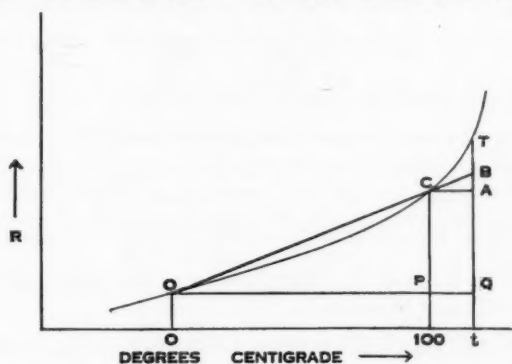


FIG. 6.

temperature,  $t$ , of steam boiling under some particular pressure other than 760 mm. of mercury. Let these ordinates meet the curve at  $O$ ,  $C$  and  $T$  respectively. Join  $OC$  and produce the line to meet the ordinate at  $(100 + \Delta t)$  at  $B$ ; draw  $CA$  and  $OPQ$  parallel to the temperature axis, intersecting the ordinates at 100 and  $100 + \Delta t$  in the points  $P$ ,  $Q$  and  $A$  as shown in the figure.

The increase in resistance due to the water boiling at a temperature of  $(100 + \Delta t)^\circ \text{C.}$  instead of at  $100^\circ \text{C.}$  ( $= \Delta R$ )  $= AT = AC \tan TCA$

$$\begin{aligned}
 &= AB \frac{\tan TCA}{\tan BCA}, \text{ since } \frac{AB}{AC} = \tan BCA \\
 &= AB \times \frac{TA}{CA} \times \frac{OP}{CP}, \text{ since } BCA = COP \\
 &= AB \times \frac{TQ - AQ}{CP} \times \frac{1}{CA} \times OP \\
 &= AB \times \left( \frac{R_t - R_0}{R_{100} - R_0} - \frac{R_{100} - R_0}{R_{100} - R_0} \right) \times \frac{1}{\Delta t} \times 100 \\
 &= AB \times \frac{(pt)_t - (pt)_{100}}{\Delta t}
 \end{aligned}$$

Since  $(pt)_t = \frac{R_t - R_o}{100 - R_o} \times 100$  by definition

$$\Delta R = AB \times \left[ \frac{\Delta(pt)}{\Delta t} \right]_{100}$$

$$AB = AC \tan BCA$$

$$= AC \tan COP$$

$$= AC \frac{R_{100} - R_o}{100}$$

$$= AC \frac{R_t - R_o}{100 + \Delta t}$$

if  $\Delta t$  is small and the curve is almost linear.

$$\therefore \Delta R = \Delta t \frac{R_t - R_o}{100 + \Delta t} \left[ \frac{d(pt)}{dt} \right]_{100} \text{ in practice.}$$

The value of  $\frac{d(pt)}{dt}$  is of course obtained by differentiating the equation

$$t - (pt) = \delta \left\{ \left( \frac{t}{100} \right)^2 - \left( \frac{t}{100} \right) \right\}$$

and substituting the values of 1.50 for  $\delta$  and 100 for  $t$ .

Turning now to the case of the boiling point of sulphur, it can be observed that this geometrical proof is not applicable in detail, since  $CP$  would have to be put equal to  $R_{444.6} - R_o$ , if the proof were followed along on entirely parallel lines:  $\frac{TQ}{CP} \times OP$  would then be  $\frac{R_{444.6 + \Delta t} - R_o}{R_{444.6} - R_o} \times 444.6$ , which could not be put equal to  $(pt)_{444.6 + \Delta t}$ . For the case of the boiling point of sulphur the following proof must be used.

Referring to Fig. 7, let  $OCDT$  represent the curve relating resistance and temperature. Draw ordinates at  $0^\circ$ , at  $100^\circ$ , at  $444.6^\circ$  and at  $(444.6 + \Delta t)^\circ \text{C.}$ ,

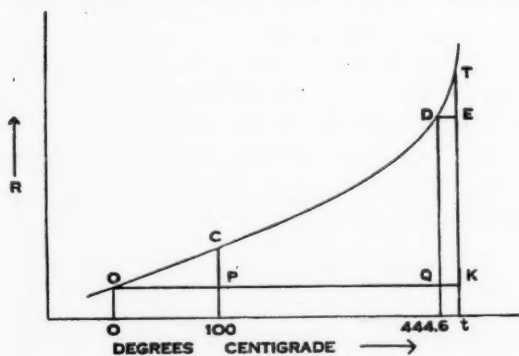


FIG. 7.

meeting the curve respectively at the points  $O, C, D, T$ . Draw parallels to the temperature axis at  $D$  and  $O$ , intersecting the ordinates as shown in the diagram at the points  $E, P, Q, K$ .

Now

$$\begin{aligned}\frac{\Delta R}{\Delta t} &= \frac{TE}{DE} = \frac{TK - EK}{DE} = \frac{TK - EK}{CP} \times \frac{OP}{DE} \times \frac{CP}{OP} \\ &= \left[ \frac{R_{444.6} + \Delta t - R_o}{R_{100} - R_o} - \frac{R_{444.6} - R_o}{R_{100} - R_o} \right] \times 100 \times \frac{R_{100} - R_o}{100} \times \frac{1}{DE} \\ &= \left[ (pt)_t - (pt)_{444.6} \right] \times \frac{R_{100} - R_o}{100} \times \frac{1}{\Delta t} \\ &= \left[ \frac{\Delta(pt)}{\Delta t} \right]_{444.6} \times \frac{R_{100} - R_o}{100}\end{aligned}$$

or  $\Delta R = \frac{R_{100} - R_o}{100} \times \Delta t \left( \frac{d(pt)}{dt} \right)_{444.6}$  for small values of  $\Delta t$ .

As for the steam point,  $\frac{d(pt)}{dt}$  is found by differentiation and substituting the value 1.50 for  $\delta$ , and 444.6 for  $t$ .

### 5. The Effect of Experimental Errors on the Value of $\delta$

The calculation of  $R_{444.6}$  is not, however, the object of measuring the resistance at the boiling point of sulphur; the object of that measurement is to obtain the  $\delta$ -value for the thermometer in question so that the substitution may be made in the formula  $t - pt = \delta \left\{ \left( \frac{t}{100} \right)^2 - \left( \frac{t}{100} \right) \right\}$ , and thus permit its use in determining temperatures in the range of the platinum thermometer.

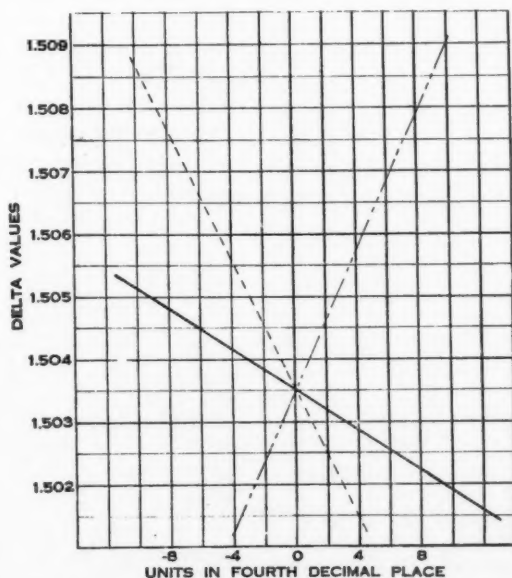


FIG. 8. Diagram showing the extent to which the delta value of a thermometer measuring 10 ohms at 0° C. is affected by errors in the fourth decimal place of resistance measurement. (a) At 0° C. ----- (b) At 100° C. - - - - - (c) At 444.6° C. ———

The accuracy of the constant  $\delta$  is thus of great importance, and as it depends on three measurements of resistance, as well as the measurement of the atmospheric pressure under which the sulphur vapor was boiling during one of

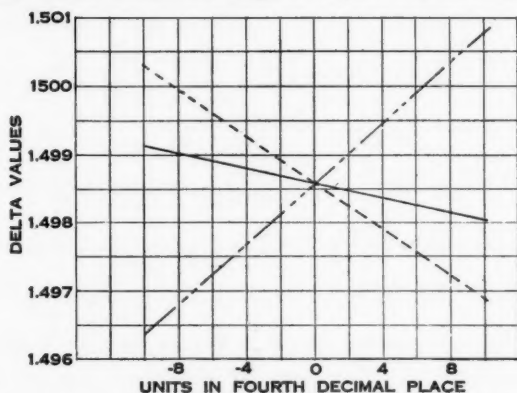


FIG. 9. Diagram showing the extent to which the delta value of a thermometer measuring 32 ohms at 0° C. is affected by errors in the fourth decimal place of resistance measurement. (a) At 0° C. ----- (b) At 100° C. -.-.-.-.- (c) At 444.6

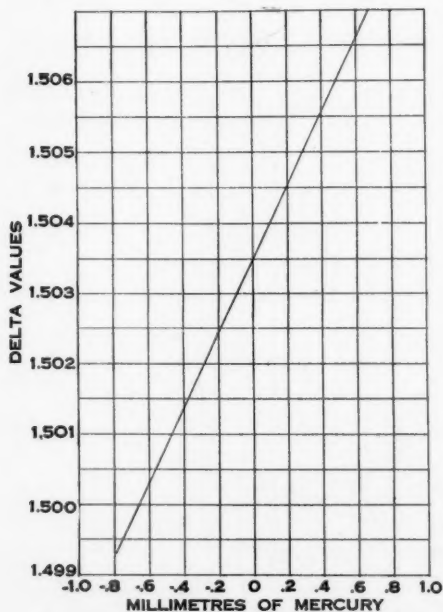


FIG. 10. Diagram showing the extent to which the delta value of a thermometer measuring 10 ohms at 0° C. is affected by errors in the barometer reading at the time at which the resistance at the boiling point of sulphur was being measured.

these resistance measurements, it is of interest to examine the effect of errors on the accuracy of the  $\delta$  value. In order to ascertain this, calculations of  $\delta$  have been made when errors in the various measurements were assumed, and the values of those obtained have been plotted against the assumed errors. These errors consisted of a certain number of units in the fourth decimal place of the resistance reading, or of a certain number of tenths of a millimetre in the atmospheric pressure reading. They were calculated for two different thermometers, whose resistances were about 10 ohms and 32 ohms, respectively, at 0° C. These small errors caused a change in  $\delta$  which for all practical purposes could be represented by a linear relation. It can be seen from Figs. 8 and 9 that an error in the fourth decimal place in the resistance reading

at the temperature of boiling sulphur changes the value of  $\delta$  by only about one-third of the amount which an error in the fourth decimal place would at the ice or steam point. As would be expected, and as demonstrated in Figs. 9 and 10, accuracy in reading the barometer in this case is relatively much more important with a thermometer of large resistance. In the case

TABLE I

DATA ON THE VARIATION OF ATMOSPHERIC PRESSURE DURING THE TIME TAKEN TO MAKE RESISTANCE MEASUREMENTS

| Interval, min. | Variation in barometric pressure, mm. | Interval min. | Variation in barometric pressure, mm. |
|----------------|---------------------------------------|---------------|---------------------------------------|
| 10             | 0.23                                  | 23            | 0.03                                  |
| 8              | 0.29                                  | 5             | 0.01                                  |
| 5              | 0.00                                  | 11            | 0.04                                  |
| 8              | 0.01                                  | 11            | 0.11                                  |
| 10             | 0.15                                  | 5             | 0.26                                  |
| 5              | 0.15                                  |               |                                       |

of the small resistance thermometer, an error of 0.1 mm. will introduce a change equivalent to about three times that introduced by an error of one in the fourth decimal place in the resistance reading in sulphur vapor; while, in the case of the 32 ohm thermometer, the corresponding change is more than nine times as great—a result that one might expect from the fact that the resistance of the one thermometer is more than three times that of the other.

The question now arises whether the barometer level varies sufficiently between readings to cause serious changes in the value of  $\delta$ . In Table I some of the actual intervals between readings are given, together with the variation in barometric pressure recorded. Clearly, it is seen from these observations that a variation of 0.2 mm. between readings is not uncommon. Reference to Fig. 11 indicates that for the 32 ohm thermometer an error of 0.2 mm. corresponds to an error of 0.00095 in the value of  $\delta$ ; such an error corresponds to an error of almost 2 in the third decimal place in resistance reading. It is, therefore, difficult to read to the fourth decimal place in resistance

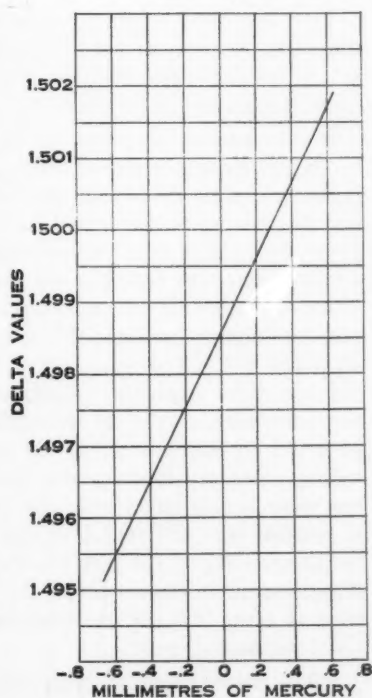


FIG. 11. Diagram showing the extent to which the delta value of a thermometer measuring 32 ohms at 0° C. is affected by errors in the barometer reading at the time at which the resistance at the boiling point of sulphur was being measured.



on those days on which the barometric pressure varies as much as 0.2 mm. during, say, an eight minute interval.

Since a variation of one unit in the third decimal place of  $\delta$  corresponds to a barometric change of about 0.2 mm., and since the formula which relates pressure and temperature—namely,

$$t_s = 444.6 + 0.0909 (p - 760) - 0.000048 (p - 760)^2$$

shows that such a barometric change corresponds to a change of about 0.018°C. in the boiling point of sulphur, it is clear that in order to obtain accuracy in the third decimal place of  $\delta$ , the temperature in the boiling tube must be held constant to two one-hundredths of a degree. As the writer observed repeatedly that at various barometric pressures the temperature variation within the boiling tube amounted to about two one-hundredths of a degree, even when the utmost precautions were taken to see that the condensation line was above the level of the insulation, the absurdity of attempting to measure  $\delta$  to the fourth decimal place is once more emphasized.

This, however, raises the question as to what part of the boiling tube is the most suitable, and throughout the work it has been assumed that it is best to use the lowest position recommended by Mueller and Burgess, namely, when the bottom of the shield is 6 cm. above the level of the liquid sulphur.

It is of interest here to note that the agreement in the literature in regard to the temperature above sulphur boiling under a pressure of 760 mm. of mercury is not good beyond the first decimal place. At the time that Mueller and Burgess published their paper on the standardization of the boiling point of sulphur, there was doubt whether 444.6 or 444.5 should be taken as the correct value; the choice made was 444.6° C. Chappuis, who published his "Détermination de la température d'ébullition du soufre" about the same time or slightly earlier, also concluded that the boiling point of sulphur should be 444.6, but remarked at the end of his communication that this value did not differ from the two values 444.51 and 444.55 found by previous experimenters, except by quantities of the order of the experimental error. It would appear that it was not easy to achieve accuracy in determining the boiling point of sulphur on the absolute scale, and, while the difficulties doubtless were largely connected with the awkwardness of air thermometry, yet it is possible that differences in the conditions inside the boiling tube itself or in the shielding of the thermometer may have been partly responsible for the disagreement in the results of the various experimenters. It is worth noting that an error of 0.05° corresponds to an error of two and a half units in the third decimal place of  $\delta$ .

While the importance of accurately knowing the absolute temperature of the boiling point of sulphur is not so great now, since the temperature 444.6 has been accepted internationally as the fixed point, thus, so to speak, standardizing the temperature scale itself, yet it is of great importance to obtain as accurate a determination of  $\delta$  as possible in order to standardize other temperatures in terms of this accepted scale. By the adoption of this scale



of temperature the errors possibly due to the use of air thermometers are eliminated, but there is still the possibility of disagreement in results owing to differences in the experimental conditions, and in view of the work described above, one is led to the conclusion that it is not advisable to attempt to extend the accuracy of the determination beyond the third decimal place, with the equipment and methods accepted as standard at the present time.

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## VIBRATIONS OF POWER LINES IN A STEADY WIND

III. THE FREE VIBRATIONS OF A HEAVY STRING<sup>1</sup>BY R. RUEDY<sup>2</sup>

## Abstract

When a long heavy wire is fastened to two supports under such a tension that it is nearly straight, the span behaves in the same manner as a stretched string, but when there is appreciable sag, standing waves form mainly in the middle portion; apart from damping, their shape is described by Hermitian polynomials, which in the case of high overtones resemble sine waves. The change in the tension along the line causes attenuation of the waves. By keeping the ratio  $(T/mg)^{1/2}$  less than about unity the span is rendered vibration-proof, at least near the ends. The natural frequency of strings of finite length depends on the zero values of the Hermitian polynomials.

## 1. Small Oscillations in the Plane of the String

When a gust of wind displaces for a moment some or all the points along a stretched wire, and alters the shape of the curve described by the wire, the tension changes by a small amount  $\Delta T$  or  $\theta$ . After a certain number of oscillations the equilibrium is restored. The acceleration of a short element of the string, of length  $d\sigma$  and mass  $md\sigma$  (Fig. 1), in a vertical direction is  $d^2y/dt^2$ , so that the corresponding component of the force which arises from the change in tension is, on the one hand, equal to  $md\sigma d^2y/dt^2$ , and, on the other, equal to the difference in the tension  $-T \sin b$  at the two ends of the element  $d\sigma$ , or equal to  $d\sigma \cdot d(T \sin b)/d\sigma$ , plus the component  $Yd\sigma$  of the external forces which may be present. The equations for the motion of the element are therefore

$$\begin{aligned} m \frac{d^2x}{dt^2} &= \frac{\partial}{\partial \sigma} \left( T \frac{\partial x}{\partial \sigma} \right) + X \\ m \frac{d^2y}{dt^2} &= \frac{\partial}{\partial \sigma} \left( T \frac{\partial y}{\partial \sigma} \right) + Y \\ m \frac{d^2z}{dt^2} &= \frac{\partial}{\partial \sigma} \left( T \frac{\partial z}{\partial \sigma} \right) + Z, \end{aligned}$$

with the equation of continuity

$$\left( \frac{\partial x}{\partial \sigma} \right)^2 + \left( \frac{\partial y}{\partial \sigma} \right)^2 + \left( \frac{\partial z}{\partial \sigma} \right)^2 = 1.$$

In the case in which the motion takes place in the plane of the curve described by the string, the equations for small displacements  $\Delta y = \eta$  along the vertical and  $\Delta x = \xi$  along the horizontal direction become, neglecting higher powers of  $\eta$  and  $\xi$  in the expansion about the equilibrium position

$$\begin{aligned} m \frac{\partial^2 \eta}{\partial t^2} &= \frac{\partial}{\partial \sigma} \left( T \frac{\partial \eta}{\partial \sigma} + \theta \frac{\partial y}{\partial \sigma} \right) = \frac{\partial}{\partial \sigma} \left( T \frac{\partial \eta}{\partial \sigma} \right) + \frac{\partial}{\partial \sigma} (\theta \sin b) \\ m \frac{\partial^2 \xi}{\partial t^2} &= \frac{\partial}{\partial \sigma} \left( T \frac{\partial \xi}{\partial \sigma} + \theta \frac{\partial x}{\partial \sigma} \right) = \frac{\partial}{\partial \sigma} \left( T \frac{\partial \xi}{\partial \sigma} \right) + \frac{\partial}{\partial \sigma} (\theta \cos b) \\ \frac{\partial x}{\partial \sigma} \frac{\partial \xi}{\partial \sigma} + \frac{\partial y}{\partial \sigma} \frac{\partial \eta}{\partial \sigma} &= 0 = \cos b \frac{\partial \xi}{\partial \sigma} + \sin b \frac{\partial \eta}{\partial \sigma}. \end{aligned}$$

<sup>1</sup> Manuscript received January 11, 1936.

Contribution from the Division of Research Information, National Research Laboratories, Ottawa, Canada.

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The direct influence of steady external forces acting upon the element  $d\sigma$  disappears from the equations. Separating the terms containing the unknown increase,  $\theta$ , in the tension  $T$ , the equations become

$$\begin{aligned}\frac{\partial}{\partial \sigma} (\theta \sin b) &= \theta \cos b \frac{\partial b}{\partial \sigma} + \frac{\partial \theta}{\partial \sigma} \sin b = T \frac{\partial^2 \eta}{\partial \sigma^2} + \frac{\partial T}{\partial \sigma} \frac{\partial \eta}{\partial \sigma} - m \frac{\partial^2 \eta}{\partial t^2} \\ \frac{\partial}{\partial \sigma} (\theta \cos b) &= -\theta \sin b \frac{\partial b}{\partial \sigma} + \frac{\partial \theta}{\partial \sigma} \cos b = T \frac{\partial^2 \xi}{\partial \sigma^2} + \frac{\partial T}{\partial \sigma} \frac{\partial \xi}{\partial \sigma} - m \frac{\partial^2 \xi}{\partial t^2}.\end{aligned}$$

For some purposes it is advisable to choose the angle  $b$  in place of the length  $\sigma$  of the arc for the independent variable (1, 2, 8, 9), but in studying oscillations the results, as will be seen, become simpler when  $\sigma$  is used.

The next step then is to express the derivatives of  $\theta \sin b$  and  $\theta \cos b$  as functions of the tension  $T$  and of the co-ordinates. The introduction of

$$\begin{aligned}\frac{\partial \xi}{\partial \sigma} &= -\tan b \frac{\partial \eta}{\partial \sigma} \\ \frac{\partial^2 \xi}{\partial \sigma^2} &= \frac{-1}{\cos^2 b} \frac{\partial b}{\partial \sigma} \frac{\partial \eta}{\partial \sigma} - \tan b \frac{\partial^2 \eta}{\partial \sigma^2}\end{aligned}$$

leads to the result:

$$\begin{aligned}\frac{\partial \theta}{\partial \sigma} &= -m \left( \sin b \frac{\partial^2 \eta}{\partial \sigma^2} + \cos b \frac{\partial^2 \xi}{\partial \sigma^2} \right) - \frac{T}{\cos b} \frac{\partial b}{\partial \sigma} \frac{\partial \eta}{\partial \sigma} \\ \theta \frac{\partial b}{\partial \sigma} &= -m \left( \cos b \frac{\partial^2 \eta}{\partial \sigma^2} - \sin b \frac{\partial^2 \xi}{\partial \sigma^2} \right) + \left( T \frac{\sin b}{\cos^2 b} \frac{\partial b}{\partial \sigma} + \frac{1}{\cos b} \frac{\partial T}{\partial \sigma} \right) \frac{\partial \eta}{\partial \sigma} + \frac{T}{\cos b} \frac{\partial^2 \eta}{\partial \sigma^2}.\end{aligned}$$

Hence

$$\frac{\partial}{\partial \sigma} (\theta \sin b) = -m \frac{\partial^2 \eta}{\partial t^2} + \frac{\partial T}{\partial \sigma} \frac{\partial \eta}{\partial \sigma} + T \frac{\partial^2 \eta}{\partial \sigma^2},$$

so that the equation governing the displacement becomes

$$m \frac{\partial^2 \eta}{\partial t^2} = T \frac{\partial^2 \eta}{\partial \sigma^2} + \frac{\partial T}{\partial \sigma} \frac{\partial \eta}{\partial \sigma}.$$

Since this equation is independent of the radius of curvature  $\partial \sigma / \partial b$ , it holds, whatever the shape of the curve described by the wire in its plane of equilibrium. The equation differs by the term containing  $d\eta/d\sigma$  from the ordinary equation for the vibrating string.

On the assumption that a solution exists in the form of a product of two functions

$$\eta(\sigma, t) = \Psi(\sigma)K(t),$$

the variables separate as follows:

$$K''(t) + \kappa^2 K(t) = 0,$$

with the solution

$$K(t) = C_1 \cos \kappa t + C_2 \sin \kappa t,$$

$\kappa$  being a constant to be determined from the conditions at both ends of the span, or from the curve that the wire describes at the moment the oscillations start. Moreover,

$$\Psi''(\sigma) + \frac{\partial T / \partial \sigma}{T} \Psi'(\sigma) + \kappa^2 \frac{m}{T} \Psi(\sigma) = 0,$$

where  $m$  may vary with  $\sigma$ . The variation of the function  $\Psi$  with respect to  $\sigma$  is the same as the variation with respect to time,  $t$ , in the equation for the

oscillation of a damped spring. It is not, however, possible in general to have the two coefficients  $T'/T$  and  $m/T$  both constant at the same time, so that the change in the amplitude of the vibrations along  $\sigma$  is more complicated than the change which the amplitudes undergo with time in the case of a damped light string to which a constant tension is applied.

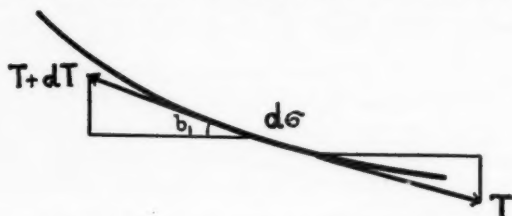


FIG. 1. The tensions acting on an element of string.

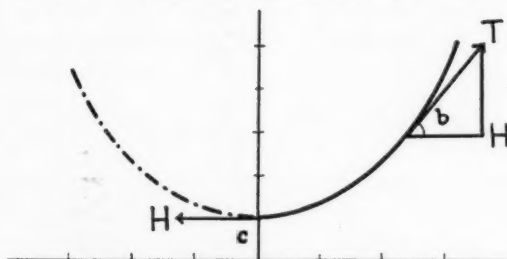


FIG. 2. Equilibrium between the tensions developing in a heavy string.

### Free Oscillations of the Catenary

When a length of wire of uniform cross section is suspended between two points which are on the same level, at a distance  $L$  from each other, each element of the wire is pulled downwards by its own weight and held back by the neighboring elements, the tension created in the wire resisting finally any further change in shape. If the wire is perfectly flexible it describes a characteristic curve, that of a catenary or an evenly loaded string to which no external tension is applied. Along this curve each element of the wire lies in the direction of the tension  $T$ , which may be considered as the resultant of a constant horizontal tension  $H$  and a vertical component equal to the weight to be supported at the element in question. Measuring  $y$ ,  $x$ , as well as the length  $\sigma$  of the arc from the lowest point in the middle of the curve, the equations of static equilibrium give (Fig. 2)

$$\sigma = \frac{H}{mg} \tan b$$

and

$$\frac{dy}{dx} = \tan b,$$

where  $b$  is the angle which the tangent at the element forms with the horizontal  $x$ -axis. The angle which the tangent makes at the fixed ends is given by

$$\tan b_0 = \frac{mg}{H} \frac{L}{2} = \sinh \frac{mg}{H} \frac{L}{2},$$

where  $S$  designates the total length of the wire supposed to remain unaltered under the tensions allowed to develop in the span. The double equation involving  $b$ ,  $L$ ,  $S$  and  $H$  determines the shape of the curve described by the wire when its mass per unit length is known. It also shows that when  $S$  is decreased for a given distance  $L$  between the supports, the horizontal tension increases according to the expression

$$\frac{dS}{dH} = \frac{2}{mg} \sinh \frac{mg}{H} \frac{L}{2} - \frac{L}{H} \cosh \frac{mg}{H} \frac{L}{2},$$

which is negative and small when the tension  $H$  is very high, as an examination of the first two terms of the series development proves, and is negative and very large when the tension  $H$  is decreased to a small value. The tangent of the curve of  $S$  against  $H$  is, therefore, negative throughout its whole range. The total tension  $T$ , on the other hand, which acts in the direction of the wire, does not necessarily decrease with a decrease in  $H$ . It is determined by the relation

$$T^2 = H^2 + (mg)^2 \sigma^2,$$

and as  $S/2$  is allowed to increase for a given value of  $L$ , the drop in  $H$  may be more than balanced by the increase in  $(mgS/2)^2$ . Differentiation of the equation for the tension  $T$  at the points of support, with respect to  $H$ , gives

$$2T \frac{dT}{dS} \frac{dS}{dH} = 2H + \frac{m^2 g^2}{2} \frac{dS}{dH},$$

and since  $dS/dH$  remains negative, there is a certain tension  $T$  for which  $dT/dS$  is equal to zero. The introduction of the value of  $dS/dH$  in the right-hand side gives in this case

$$\frac{mg}{2} \frac{L}{H} \tanh \frac{mg}{2} \frac{L}{H} = 1$$

or

$$\frac{mg}{2} \frac{L}{H} = 1.2$$

and

$$b_0 = 56\frac{1}{2}^\circ.$$

Power lines are never strung with so large an angle at the ends, since this procedure would create a sag equal to one-third of the length  $L$ , and in practice a decrease in  $H$  always lowers the value of  $T$  at the point of attachment.

The equation for  $T$  shows that for the catenary the attenuating factor  $T'/T$  depends on  $\sigma$ :

$$T = H/\cos b \text{ and } \partial T/\partial \sigma = mg \sin b,$$

so that the distribution of the amplitudes along  $\sigma$  is given by the equation

$$\Psi''(\sigma) + \frac{mg}{H} \sin b \cos b \Psi'(\sigma) + \kappa^2 \frac{m}{H} \cos b \Psi(\sigma) = 0.$$

For very taut spans, the angle  $b$  remains so small that  $\sin b$  almost vanishes along the span, and the wire behaves exactly like a string to which the constant tension  $H$  is applied. When the value of  $b$  is larger, but does not exceed about  $20^\circ$  at the ends of the span, the sine may be replaced by the main term of

$$\sin b = \frac{\tan b}{\sqrt{1 + \tan^2 b}} = \frac{mg\sigma/H}{\sqrt{1 + (mg\sigma/H)^2}},$$

while the cosine may still be regarded as equal to unity; the equation for  $\Psi$  becomes therefore

$$\Psi''(\sigma) + \left(\frac{mg}{H}\right)^2 \sigma \Psi'(\sigma) + \frac{\kappa^2}{g} \frac{mg}{H} \Psi(\sigma) = 0.$$

A change in the dependent variable  $\Psi = y_1 v$ , where

$$y_1 = e^{-\frac{\gamma}{2} \sigma^2},$$

$\gamma$  being equal to  $mg/H$ , the reciprocal of the constant  $c$  of the catenary, leads to the relation

$$\frac{d^2 v}{d\sigma^2} - \gamma^2 \sigma \frac{dv}{d\sigma} + \left(\kappa^2 \frac{\gamma}{g} - \gamma^2\right) v = 0.$$

A change from the independent variable  $\sigma$  to the dimensionless variable  $\beta = \gamma \sigma = \sigma/c = \tan b$  gives finally (5)

$$v''(\beta) - \beta v'(\sigma) + \left(\frac{\kappa^2}{g\gamma} - 1\right) v(\sigma) = 0,$$

an equation occurring also in the quantum mechanics of the harmonic oscillator, and of the same type as that valid for the functions known as Hermitian polynomials

$$H_m''(x) - x H_m'(x) + m H_m(x) = 0,$$

providing that

$$\frac{\kappa^2}{g\gamma} = m + 1.$$

It is known that when an attempt is made to solve the differential equation for  $v$  by means of a power series

$$v = a_0 + a_1 \beta + a_2 \beta^2 + \dots + a_n \beta^n + \dots,$$

the recursion formula connecting successive coefficients is

$$a_{m+2} = \frac{\frac{\kappa^2}{g\gamma} - 1 - m}{(m+1)(m+2)},$$

which shows that when

$$\kappa^2 = (m+1)g\gamma$$

the coefficient  $a_{m+2}$  vanishes, and the solution for  $v$  reduces to a polynomial of the  $n$ th degree. For other values of  $\kappa^2$  the solution is a sum of an even function and an odd function, both defined by infinite power series. Both tend to infinity at the same rate as the function  $(\exp)\beta^2/2$  for large values of  $\beta$ , so that the values specified for  $\kappa^2$  are, for long lines, the only proper constants ensuring a physical meaning of the solution. In contrast to the ordinary long string on which standing waves of any frequency may form, the standing waves developing on long heavy spans are restricted to those frequencies for which  $\kappa^2 = (m+1)g\gamma$ .

The displacement at any point of the string is given by

$$\Psi = y_1 v = e^{-\frac{\gamma}{2} \sigma^2} H_m(\gamma \sigma),$$

or, since

$$H_m(\gamma \sigma) = (-1)^m e^{\frac{\gamma}{2} \sigma^2} \frac{d^m e^{-\frac{\gamma}{2} \sigma^2}}{d(\gamma \sigma)^m},$$

$$\Psi(\sigma) = (-1)^m \frac{d^m e^{-\frac{\gamma}{2} \sigma^2}}{d(\gamma \sigma)^m}.$$

Neat standing waves form only in the middle portion; toward the points of support the motion vanishes (Fig. 3). The number of nodes is equal to  $m$ ; they lie within the section (Figs. 3 and 4)

$$-\sqrt{4m+2} < \gamma\sigma < +\sqrt{4m+2}.$$

For strings of finite length the same solutions are valid; but when the ends of the string remain fixed, its length must be taken equal to the distance

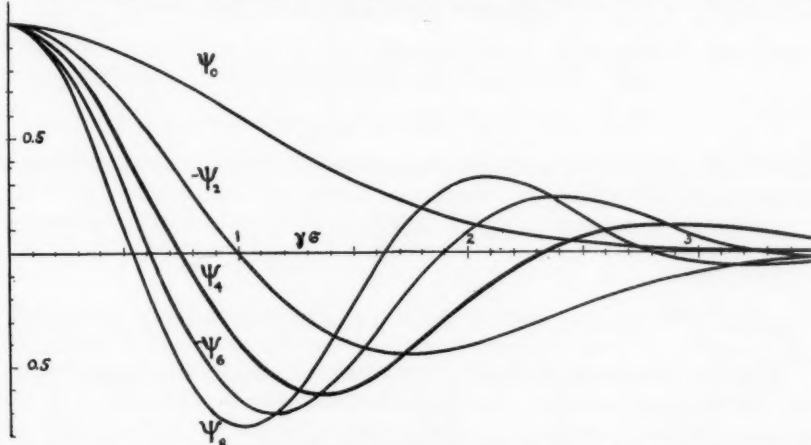


FIG. 3. Shape of standing waves on a string in which the weight of the elements is no longer negligible compared to the tensions developed. The scale has been so chosen that all the curves pass through  $\psi=1$  at the origin, so that the curves represent  $\psi_0$ ,  $\psi_2$ ,  $\psi_4/5$ ,  $\psi_6/15$  and  $\psi_8/105$ ; they are symmetrical to the  $\psi$ -axis.

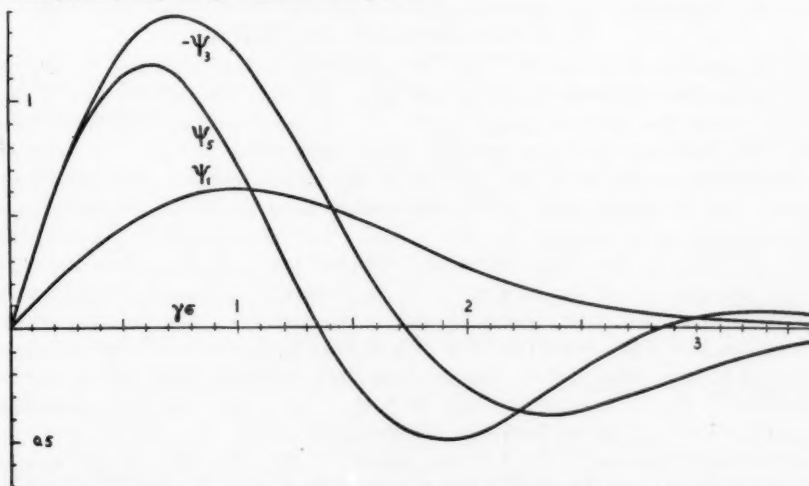


FIG. 4. Shape of standing waves on a heavy string, for the harmonics with an odd number. The ordinates of  $\psi_6$  have been divided by 3. The shape is determined by

$$(-1)^m \frac{d^m \epsilon^{\frac{\gamma^2 \sigma^2}{2}}}{d(\gamma\sigma)^m}.$$



between those points for which the value of the polynomial passes through zero, a condition which determines the response of the string at resonance. A relation holds between the shapes of the standing waves corresponding to successive overtones, namely, when  $D^m(x)$  is written for  $d^m \epsilon^{-x^2/2} / dx^m$ ,

$$(-1)^{m+1} D^{m+1}(x) = x D^m(x) - m D^{m-1}(x),$$

for instance

$$\frac{d^6 \epsilon^{-x^2/2}}{dx^6} = \epsilon^{-x^2/2} (x^6 - 15x^4 + 45x^2 - 15) = x D^5 - 5 D^4$$

$$\frac{d^7 \epsilon^{-x^2/2}}{dx^7} = -\epsilon^{-x^2/2} (x^7 - 21x^5 + 105x^3 - 105x) = -(x D^6 - 6 D^5)$$

$$\frac{d^8 \epsilon^{-x^2/2}}{dx^8} = \epsilon^{-x^2/2} (x^8 - 28x^6 + 210x^4 - 420x^2 + 105) = x D^7 - 7 x D^6.$$

When  $m$  is a very large number, the displacements of the points where standing waves are formed and for which

$$\sin \varphi = \frac{|\gamma \sigma|}{\sqrt{4m+2}} < 1$$

is given by

$$\Psi(\sigma) = \epsilon^{-\frac{\gamma^2 \sigma^2}{2}} H_m(\gamma \sigma) \doteq \epsilon^{-\frac{\gamma^2 \sigma^2}{4}} \frac{\sqrt{2m+1} \epsilon^{-\frac{m}{2}}}{\sqrt{\cos \varphi}} \cos \left( \left( m + \frac{1}{2} \right) \left( \varphi + \sin \varphi \cos \varphi - m \frac{\pi}{2} \right) \right).$$

When, finally,  $b$  reaches large values along the span, the equation for  $\Psi$  is altered so as to have  $b$  as the independent variable; in this case

$$\frac{d^2 \Psi}{db^2} - \tan b \frac{d\Psi}{db} + \frac{\kappa^2}{g \gamma \cos^3 b} \Psi = 0,$$

a differential equation of the second order in which the coefficients are periodic functions of the independent variable (Hill's equation).

### Small Oscillations of the Cycloid

The tensions at which the wires are strung on power lines are usually so high that the weight of each half-span produces only a small increase in the tension near the points of support, the catenary approaching a parabola, and the wire oscillates almost as readily as a string. (For instance, if a copper conductor is strung between supports at the same elevation, spaced 400 ft. apart, and the tensile stress is 28,000 lb. per sq. in. at the centre, the maximum stress at the ends is 28,011 lb. per sq. in.). In order to reduce the effect of the vibrations at the ends, attempts have been made to strengthen the wire near the support, in the simplest case by fastening a second piece of wire securely to the first over a certain length of the span (7). The question arises, therefore, how a line would behave with respect to oscillations if its thickness increased from the middle toward the end of each span, so that the tension  $T$  would increase rapidly with  $\sigma$ . From the equations ensuring equilibrium at any point between the tension  $H$  at the lowest point and the horizontal component  $T \cos b$  of the tension  $T$ , and also between the weight to be supported and the vertical component  $T \sin b$  of the tension  $T$ , it follows since the weight is equal to  $m_0 \int_0^\sigma \rho_0(\sigma) d\sigma$ , that

$$H \tan b = g m_0 \int_0^\sigma \rho_0(\sigma) d\sigma.$$

A simple expression results if  $\rho_o(\sigma)$  be so chosen that  $H \tan b = g m_o \sigma / \cos b$ , or  $m_o g \sigma = H \sin b$ . The condition

$$\int_0^\sigma \rho_o(\sigma) d\sigma = \frac{\sigma}{\cos b} = \frac{\sigma}{\sqrt{1 - \sigma^2/C_o^2}} = \frac{C_o \sigma}{\sqrt{C_o^2 - \sigma^2}}$$

is fulfilled by

$$\rho_o(\sigma) = \frac{C_o^2}{\sqrt{(C_o^2 - \sigma^2)^3}} = \frac{1}{(\cos b)^{\frac{3}{2}}}.$$

When the mass of unit length increases according to this law from the middle of the span toward the ends, a flexible wire describes the curve

$$\sigma = \frac{H}{m_o g} \sin b = C_o \sin b,$$

a cycloid, such as would be traced by a point on the rim of a circle of diameter  $C_o/2$  rolling along the lower side of a straight wire connecting the points of suspension. The tension  $T$  is determined by the equation

$$T^2 = H^2 + \frac{m_o^2 g^2 \sigma^2}{\cos^2 b} = \frac{H^2}{\cos^2 b}.$$

The tension  $T$  acting at any point  $\sigma$  in the direction of the cycloid is therefore given by the same formula as that giving the tension acting in the catenary, and the tensions are practically the same so long as  $\sigma = C_o \tan b$  may be replaced by  $\sigma = C_o \sin b$ . Furthermore, over the same range, the free oscillations of the catenary are governed by the same equations as those produced along the catenary. When the spans are so constructed as to have equal strength at the ends, the highest tension developing in the cycloid span will, however, be smaller than that obtained in the catenary. Increasing the thickness of the wire toward the ends results therefore in a saving of material.

### Vibration-proof Spans

When  $\gamma\sigma$  is very large a simple solution may be obtained directly from the initial equation

$$\Psi''(\sigma) + \gamma^2 \sigma \Psi'(\sigma) + \frac{\kappa^2}{g} \gamma \Psi(\sigma) = 0$$

by putting

$$\Psi = \gamma_1 v$$

with

$$\gamma_1 = e^{-\int \gamma^2 \sigma d\sigma} = e^{-\frac{\gamma^2}{2} \sigma^2}$$

in order to remove the first derivative. The differential equation becomes

$$\frac{d^2 v}{d\sigma^2} + \left( \frac{\kappa^2}{g} \gamma - \frac{\gamma^2}{2} - \frac{\gamma^4}{4} \sigma^2 \right) v = 0.$$

When  $\sigma^2 \gamma^4/4$  is larger than all the other terms in the bracket, the expression reduces to

$$\frac{d^2 v}{d\sigma^2} - \frac{\gamma^4}{4} \sigma^2 v = 0,$$

or in operator notation

$$(D + \gamma^2 \sigma/2)(D - \gamma^2 \sigma/2)v = 0,$$

or

$$\frac{dv}{d\sigma} \pm \frac{1}{2} \gamma^2 \sigma v = 0.$$

Hence

$$v = A_1 e^{-\frac{\gamma^2}{4}\sigma^2} + A_2 e^{+\frac{\gamma^2}{4}\sigma^2}$$

$$\Psi(\sigma) = A_1 e^{-\frac{\gamma^2}{4}\sigma^2} + A_2,$$

where  $A_1$  and  $A_2$  are two constants depending on the initial conditions. When the two ends are fixed  $A_2 = 0$ , and the disturbance becomes rapidly attenuated as it progresses along the line. Standing waves are unable to form on the wire which is practically prevented from transmitting vibrations.

Now the conditions for having  $\gamma^4 \sigma^2 / 4$  large compared to  $\kappa^2 \gamma / g$  are the same as those for having  $T'/T$  much larger than  $\kappa^2 m/T$ , or for the catenary,

$$mg \frac{\sigma}{H} \gg \frac{\kappa^2}{g}.$$

By taking points which are sufficiently far from the origin,  $\sigma$  can be given very large values so that the condition for a vibration-proof cable is fulfilled whenever

$$\frac{mg}{H} > \frac{\kappa^2}{g}.$$

For vibrations excited by the wind,  $\kappa$ , the number of the nodes, is at least equal to 30, so that  $mg/H$  or, what is nearly the same,  $mg/T$ , must at least be greater than unity, or  $(T/mg)^{1/2} < 1$ , approximately.

A study recently made (3, 4) of about 40 transmission lines in a dozen different countries has indeed revealed that, roughly speaking, for reasons not then apparent, a line is unaffected by vibration when  $(T/mg)^{1/2} < 1/3$ , approximately.

The mathematical theory of the forces in spans with varying tension agrees therefore on the whole with the results furnished by experience in the field. It is, of course, a matter of common knowledge that the use of lower tensions renders spans less subject to vibrations.

Slight improvements are obtained by merely strengthening the ends. A drastic reduction in the tension of the conductor without an increase in the sag is possible when the tightly stretched core of the wire supports the loosely fitting envelope which has merely to carry current; under these conditions the portion of the line exposed to the action of the wind cannot respond to the eddy frequencies (6).

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# Canadian Journal of Research

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## THE SYNTHESIS OF $\delta$ -(3-INDOLYL)-VALERIC ACID AND THE EFFECTS OF SOME INDOL ACIDS ON PLANTS<sup>1</sup>

BY RICHARD H. F. MANSKE<sup>2</sup> AND LEONARD CHRISTIE LEITCH<sup>3</sup>

### Abstract

The synthesis of  $\delta$ -3(indolyl)-valeric acid, by a procedure analogous to that employed in the synthesis of its lower homologues, is described. It, as well as a  $\beta$ -methyl derivative of  $\beta$ -3(indolyl)-propionic acid, which has also been synthesized, was found to possess the plant physiological properties of a phytohormone.

The isolation of indolyl-3-acetic acid from a number of natural sources and its recognition as a phytohormone of remarkable potency (5, 6) has led to the study of a large number of compounds, many of which may be classed in this group. Indolyl-propionic and -butyric acids are examples of this, and in order to extend our knowledge of this series the synthesis of the homologous  $\delta$ -(3-indolyl)-valeric acid was undertaken. Dr. Percy W. Zimmerman of the Boyce Thompson Institute, Yonkers, New York, has kindly examined the synthetic acid and the following résumé of the subject has been written by him at our request.

"The term 'phytohormone' has been used in connection with substances which induce formative effects on plants. In the earlier days only substances (auxins) produced by the plants themselves were considered under this head, but we now know many synthetic compounds should be included in the same category. The principal responses of plants to the application of these growth substances are acceleration of growth and initiation of new organs.

"The indole compounds have a large number of homologues which are especially interesting as growth substances. Through the kindness of Dr. R. H. Manske, I have had the opportunity of testing sixteen new compounds (10). Of these, four have been found physiologically effective. They are as follows:  $\gamma$ -3(indolyl)-butyric acid,  $\delta$ -3(indolyl)-valeric acid,  $\beta$ -3(5-methyl-indolyl)-propionic acid and indylene-1:3 diacetic acid (4). Dr. A. E. Hitchcock (2) of this laboratory had previously tested and found effective  $\beta$ -3(indolyl)-propionic acid which Dr. Manske prepared.

"These substances may be applied to plants as water solutions or as preparations mixed with lanolin. When applied in water the response of the

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plant is inclined to be systemic whereas the lanolin preparation of low concentration applied locally causes a local response. The water solution can be added to the soil or injected with glass tubes drawn to a capillary at one end (Fig. 2). The tube is filled with the substance (about 0.3 cc.) and then the capillary end inserted into a stem or petiole and left to drain into the plant. A concentration of 10 parts of indolyl-butyric acid per million of water was found very effective. Higher concentrations were necessary when the substance was added to the soil or was mixed with lanolin. The solutions can be applied to either the roots or stems. The material makes its way into the vascular system and if the concentration is high enough the entire plant responds. Fig. 1 shows the effect of an application along one side of an active stem. Growth is accelerated locally where the material goes into the tissue and the increased length causes bending and curling. For acceleration of growth indolyl-acetic acid is the most effective substance, followed in order by indolyl-butyric, indolyl-propionic, indolyl-valeric, 5-methyl-indolyl-propionic, and indylene-1:3-diacetic acid. The last two are only slightly effective as compared with the other four.

"Figure 2 shows the results with indolyl-butyric injected as a water solution. Figure 3 shows the results from a local application of indolyl-acetic acid (2 per cent in lanolin). Indolyl-butyric acid and naphthyl-acetic acid are the most powerful root forming substances known. Indolyl-acetic acid is next in order, followed by indolyl-propionic, phenylacetic, and indolyl-valeric acid.

"The roots induced by these compounds appear normal and when treated stems are cut off and put into soil they grow as normal plants. From the results to date it seems certain that practical applications can be made to plant propagation. Also, teachers of plant physiology will find these compounds interesting and useful for experimental work."

The synthesis of the acid named in the title was achieved by an application of the Fischer indol synthesis to the phenylhydrazone of  $\alpha$ -keto-suberic acid and the subsequent elimination of carbon dioxide from the resulting dibasic acid. The synthesis is strictly parallel to that of the two lower homologues (3, 8), and in this case too the phenylhydrazone was obtained by means of the Japp-Klingemann reaction from the homologous ethyl cyclo-heptanone-carboxylate. The last was prepared by the method first used by Kötze and Michels (7) for the synthesis of ethyl cyclohexanone-carboxylate. The cycloheptanone was obtained by the excellent procedure recently placed on record by Mosettig and Burger (9).

### Experimental

#### *Ethyl Cycloheptanone-2-carboxylate*

A mixture of 52 gm. of suberone (9) and 75 gm. of ethyl oxalate was added gradually to a cooled solution of sodium ethylate (11 gm. of sodium in 150 cc. of absolute alcohol). The reaction mixture was allowed to remain for three days in a cold place and then acidified with ice-cold diluted hydrochloric acid.

PLATE I



FIG. 1. Jerusalem artichoke (*Helianthus tuberosus*) showing response to synthetic growth substances. Left, two shoots as controls. Right, one control and three shoots treated along one side with lanolin preparations (1%) of indolyl-acetic, indolyl-butyric, and indolyl-propionic acid. The bending due to acceleration of growth where the substance was applied can be seen 30 min. after its application.

FIG. 2. Tomato plants. Left, control. Right, plant injected with 0.01% of indolyl-butyric acid, which caused epinasty of leaves, bending of stem, and initiation of roots on leaf and stem. Roots could be seen five days after treatment.

FIG. 3. Tomato stem with a local application of a 2.0% lanolin preparation of indolyl-acetic acid, showing masses of roots initiated by the substance. Other indol compounds act similarly.





The golden yellow oil that separated was taken up in ether, the ethereal solution washed with sodium carbonate and dried over sodium sulphate. After being freed of solvent the residue was fractionated under reduced pressure. When evolution of carbon monoxide had ceased, a small, low-boiling fraction was collected from which some suberone was recovered. The cyclic ester distilled between 135°–145°C./30 mm. Refractionation of this product yielded the pure ethyl cycloheptanone-2-carboxylate; b.p. 135°–138° C./22 mm.; yield, 36 gm.

*$\delta$ -3(2-Carboxy-indolyl)-valeric Acid*

A solution of benzene-diazonium chloride prepared from 15 gm. of aniline was gradually added to an iced solution of 36 gm. of ethyl cycloheptanone carboxylate in 200 cc. of 20% potassium hydroxide. Toward the end of the addition a further small amount of potassium hydroxide was added to keep the acidic products in solution. After one hour in the ice chest the intense red solution was acidified with cold dilute hydrochloric acid and the resinous precipitate washed with water by decantation.

The phenylhydrazone of  $\alpha$ -keto-suberic acid thus obtained was dried in an oven at 60° C. and then heated under reflux for a short time with 150 cc. of absolute alcohol containing 20 cc. of concentrated sulphuric acid. On cooling, a considerable amount of ammonium sulphate crystallized out. The latter was removed by filtration and the filtrate heated under reflux for one hour. The cooled filtrate was diluted with much ether and the solution thoroughly washed with water, then with aqueous sodium bicarbonate, and dried over sodium sulphate. Removal of the ether yielded a pale brown syrupy residue which deposited a small amount of colorless crystalline material in the course of several days. This was filtered off, washed with benzene and recrystallized from hot methanol in which it is sparingly soluble. As thus obtained it consisted of colorless glistening needles, melting sharply at 170° C.\*. Yield, 3.2 gm. Although this substance gives an intense red color with Ehrlich's reagent its nature is still obscure to the authors. Calcd. for  $C_{29}H_{34}O_7N_2$ : C, 66.67; H, 6.51; N, 5.36%. Found: C, 66.48; H, 6.61; N, 5.29%. (Mean of two concordant analyses.)

The prolonged action of methanolic hydrazine on this substance at steam bath temperatures yielded a product, insoluble in water, which, when recrystallized from methanol in which it is moderately soluble, melts at 146° C. and still gives Ehrlich's reaction for indols. The complete loss of oxygen in this reaction does not serve to elucidate the nature of the substance. Calcd. for  $C_{25}H_{30}N_2$ : C, 83.80; H, 8.38; N, 7.82%. Found: C, 83.97; H, 7.97; N, 7.82%.

The benzene filtrate from the above-described substance (m.p. 170° C.) was freed of solvent, finally *in vacuo*, and the residue (34 gm.) was heated on the steam bath with 30 gm. of potassium hydroxide in aqueous methanol. Water was added and the organic solvents removed by evaporation. A small

\*All melting points are corrected.

amount of unsaponifiable material was removed by thorough extraction with ether (the ether solution yielded a further small amount of the above-mentioned unidentified substance; m.p. 168–170 °C.). The ether was boiled out of the aqueous solution and the latter acidified with dilute hydrochloric acid to an incipient permanent turbidity. The filtered solution (charcoal) was acidified with hydrochloric acid, and, after cooling, the crystallized acid was filtered off, washed with water and dried; yield, 22 gm. A small portion was recrystallized by adding chloroform-benzene to a concentrated methanol solution. After filtering and washing with chloroform,  $\delta$ -3(2-carboxy-indolyl)-valeric acid was obtained in colorless fine needles melting sharply but with evolution of carbon dioxide at 204° C. Borsche and Manteuffel (1), who obtained this acid incidentally to other work, give the m.p. as 193–195° C. It is pertinent to note that the corresponding butyric acid (3) when recrystallized from dilute alcohol also melts at 204° C., but a mixture of equal amounts is completely liquid at 185–187° C. Calcd. for  $C_{14}H_{18}O_4N$ : C, 64.37; H, 5.75%. Found: C, 63.99; H, 5.74%.

#### *Isolation of Pimelic Acid*

The aqueous filtrate from the above-mentioned acid was evaporated to dryness on a steam bath, and the residue dissolved in the minimum amount of water. Some insoluble material was removed by filtration with charcoal, and the filtrate was extracted with ether. Removal of the solvent and recrystallization of the residue from hot water yielded colorless fine prisms which after drying melted sharply at 106° C. Since the corresponding solution from the preparation of  $\gamma$ -3(2-carboxy-indolyl)-butyric acid yielded adipic acid, the acid under consideration should be pimelic acid, and this was confirmed by mixed melting point determinations with an authentic specimen.

In the case of the analogous propionic acid (*vide infra*) a small amount of glutaric acid was obtained from the corresponding solution. The formation of these acids is evidently not to be ascribed to a possible contamination of the cyclic keto-esters. Their immediate precursors are probably the  $\alpha$ -keto-acids formed as the result of the hydrolysis of the phenylhydrazones, since phenylhydrazine has been isolated from the aqueous solution of the indol-ring closure reaction in the case of the -butyric acid. The action of the hot alkali on the  $\alpha$ -keto-acids could conceivably result in oxidative elimination of carbon dioxide.

#### *$\delta$ -3(Indolyl)-valeric Acid*

The dibasic acid (18 gm.) was heated in an oil bath to 210° C. (inside temperature) until evolution of carbon dioxide ceased. The cooled melt was extracted with aqueous sodium bicarbonate and the turbid solution exhausted with ether. The resulting clear aqueous solution was acidified with hydrochloric acid and the liberated acid extracted with ether. The washed and dried (sodium sulphate) ethereal solution was freed of solvent. The residue (11 gm.) solidified completely on cooling but it was nevertheless difficult to obtain the pure acid from this by crystallization. It was converted to the

methyl ester by heating under reflux for four hours with 100 cc. of methanol containing a small amount of dry hydrogen chloride. The ester was isolated in the usual way and distilled *in vacuo*. There was obtained 9 gm. of colorless oil, b.p.  $210^{\circ}$  C./2 mm., which solidified completely on cooling. A small portion was crystallized with difficulty from benzene-petroleum ether. Methyl  $\delta$ -(3-indolyl)-valerate was thus obtained in large flat plates melting at  $57^{\circ}$  C. Calcd. for  $C_{14}H_{17}O_2N$ : N, 6.06%. Found: N, 6.64%.

The above-mentioned methyl ester (8 gm.) was hydrolyzed with methanolic potassium hydroxide, and the acid isolated by ether extraction of the clarified (charcoal) and acidified solution. The residue from the washed and dried ether solution was dissolved in a small amount of hot benzene. On cooling, the acid crystallized readily. A small amount of petroleum ether was added to facilitate filtration. The acid was washed first with benzene-petroleum ether and then with the latter. As thus prepared  $\delta$ -(3-indolyl)-valeric acid melts at  $105^{\circ}$  C. Yield, 6 gm. Calcd. for  $C_{13}H_{15}O_2N$ : C, 71.89; H, 6.91; N, 6.45%. Found: C, 72.11; H, 7.09; N, 7.04%.

#### $\beta$ -(5-Methyl-indolyl)-propionic Acid

A small quantity of this acid was required for reasons mentioned in the introduction. The now well known procedure, starting with *p*-toluidine in this case and ethyl cyclopentanone-carboxylate, was employed. The intermediates were not purified and details appear unnecessary. The acid was purified *via* the methyl ester and recrystallized from hot water, whence it was obtained in clusters of fine white needles which melted sharply at  $137^{\circ}$  C. For reasons not obvious the yield was only meagre. Calcd. for  $C_{12}H_{13}O_2N$ : C, 70.93; H, 6.40; N, 6.90%. Found: C, 70.82; H, 6.35; N, 7.07%.

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## THE ALKALOIDS OF *SENECIO* SPECIES

### II. SOME MISCELLANEOUS OBSERVATIONS<sup>1</sup>

BY RICHARD H. F. MANSKE<sup>2</sup>

#### Abstract

Some miscellaneous observations on the alkaloids of *Senecio* species are brought together. Of the nine species here reported upon, only four, namely: *S. mikanioides*, *S. aureus*, *S. solidago* and *S. cineraria*, yielded tractable amounts of alkaloids. The first gave amorphous *mikanoidine*,  $C_{21}H_{19}O_4N$ , which on hydrolysis yielded a base, *mikanecine*,  $C_8H_{10}O_2N$  and *mikanecic acid*,  $C_{13}H_{16}O_4$ . *S. aureus* yielded *aureine*,  $C_{19}H_{25}O_5N$ , which is distinguished by its high melting point ( $238^\circ C.$ ) from known alkaloids of this genus. All species so far examined yielded *fumaric acid*. Some observations which may aid in elucidating the structure of *retronecine* are recorded.

Owing to the pressure of other work and to a shortage of starting material, it has been possible for the author to continue work on the alkaloids of *Senecio* species only at intervals. Subsequent to the publication of the first paper (4) several investigators have placed on record relevant communications (1, 5, 7), and since there is the possibility of duplication, the author takes this opportunity of publishing some miscellaneous observations.

It is now fairly well established that the alkaloids of *Senecio* are *alkamine esters*<sup>\*</sup>, and in several cases at least the basic fragment consists of *retronecine*. The alkaloid of *Senecio vulgaris* L. can be added to this group. The *necic acid* was difficult to purify though it was obtained crystalline. However, since Professor Barger (private communication) has stated his intention to include this plant in his investigations, its further examination was abandoned.

*S. mikanioides*, (Walp.) Otto, of New Zealand origin was found to yield a very small amount of alkaloid which could not be crystallized, but which on hydrolysis yielded a base, *mikanecine*, characterized as *picrate*, and *mikanecic acid*, both of which appear to be new. *S. solidago*, Rydb. collected in Northern Montana, U.S.A. yielded a very small amount of non-crystallized base which on hydrolysis yielded the expected acid and basic fragments, but sufficient for characterization was not available. The author had previously recorded the probable absence of alkaloids in *S. aureus* L., but a collection made in Alberta yielded a small quantity of well crystallized base whose analytical figures are in substantial agreement with the formula  $C_{18}H_{23}O_5N$ .

Several other species obtained from the Arboretum of the Dominion Experimental Farm, Ottawa, through the courtesy of Mr. John Adams, were investigated. With the exception of the first, the following were found to be

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\*In this connection it is pertinent to note that the disputed presence of an alkaloid in *Echium vulgare*, L. (3) has been confirmed. Though present only in traces and not obtained crystalline, hydrolysis of the amorphous alkaloid yielded an unstable basic fragment together with *tiglic acid*.

virtually devoid of alkaloidal constituents of which the quantities indicated were examined; *S. cineraria*, DC. (138 gm.), *S. clivorum*, Maxim. (126 gm.), *S. nemorensis* L., (640 gm.) (5), *S. veitchianus*, Hemsl. (65 gm.), *S. palmatus*, Pall. (150 gm.) and *S. ledebouri*, Sch. Bip. (210 gm.). It is of interest to note that all *Senecio* species (12 in number) investigated by the author, yielded fumaric acid, while the isolation of quercetin from *S. jacobaea* may now be reported.

Hoffmann degradation of retrorsine has yielded some products which may be of value in connection with the constitution of retronecine. Treatment of the methiodide in hot aqueous solution with silver oxide readily yielded the methohydroxide, which on careful decomposition yielded a product soluble in chloroform and presumably consisting of the methine base. The second stage of the process, as might indeed have been anticipated, did not proceed normally. The addition of methyl iodide to the methine in chloroform proceeded readily enough, but the product was not the simple methiodide. Scission of the molecule ensued and an ether-soluble ester of retronecic acid ( $C_{13}H_{15}O_6$ ) together with a methiodide was formed. The former reduces Fehling's solution and yields the odor of iodoform when heated with iodine in potassium carbonate solution. Neither of these reactions is given by retronecic acid, so that these properties must be ascribed to the alcohol, the empirical formula of which is therefore  $C_9H_{11}O_2$ . Hydroxy-acetone and  $\alpha$ - and  $\beta$ -hydroxy-propionaldehyde are the only reasonable possibilities, but the former was eliminated because synthetic acetol retronecate was not identical with the new esters. Further, it is doubtful whether  $\beta$ -hydroxy-propionaldehyde would give the iodoform reaction. The ester is therefore provisionally regarded as  $\alpha$ -hydroxy-propionaldehyde retronecate, although other possibilities are not improbable. The methiodide was complex but on treatment with silver oxide yielded a small amount of a crystalline substance, the analytical figures of which are in accord with the formula  $C_9H_{11}O_2N$ . This compound has the properties of a betaine, including a pronounced saccharine taste. It does not react with methyl iodide and is neutral to litmus. That a portion of the molecule of retronecic acid is not present was proved by the observation that the same compound can be obtained by a similar degradation of benzoyl retronecine. It does not give a color with Ehrlich's reagent until after partial decomposition by heat. It therefore still retains the potential pyrrol nucleus of the parent base. Confirmatory evidence from other sources does not warrant the postulation of a structural formula for retronecine on this basis. It nevertheless appears that a carbon atom, as well as a number of hydrogens, was lost by oxidation.

### Experimental

#### Isolation of Alkaloids

In all cases the following procedure was adopted with but negligible modifications. The methanolic extract was freed as far as possible of the solvent by evaporation on the steam bath. Water was added and the remainder of the methanol boiled off. The mixture was then rendered acid to congo red



by the addition of hydrochloric acid and set aside for several days, finally in the ice chest. The aqueous solution could then be readily decanted from the insoluble material and clarified by filtration through a layer of charcoal.

The aqueous layer was then exhausted with ether and in all cases fumaric acid, identified by melting point and mixed melting point, was isolated from the ether extract, purification being effected by recrystallization from water. In the case of *S. jacobaea* the ether extract also contained quercetin (m.p. 230–231° C.)\* which was further identified by comparing its tetramethyl ether (m.p. 159–160° C.) and the pentacetate (m.p. 194° C.) with authentic specimens. The aqueous solution was then basified with ammonia and again exhausted with ether. The residue from this ether extract was further purified by dissolving in dilute hydrochloric acid, extracting the filtered solution with ether, basifying with ammonia and extracting again. In addition to the three cases specifically mentioned below only *S. cineraria* and *S. solidago* yielded definitely recognizable amounts of alkaloid from the quantities of material available.

#### *S. vulgaris* L. \*

At various times limited supplies of this plant were available for examination. The yield of crystalline alkaloid varied between 0.15 and 0.17%. After repeated crystallization it melted to a dark tar at 222° C. This is evidently the senecionine of Grandval and Lajoux (2). Admixture with a pure specimen of jacobine (m.p. 222–224° C.) caused a depression in melting point of at least 12°. Calcd. for  $C_{18}H_{23}O_8N$ : C, 64.86; H, 6.91; N, 4.20%. Found: C, 63.04; H, 7.20; N, 4.26%.

Since other investigators have also reported the difficulty of burning these bases, the low value for carbon is not unreasonable. Nevertheless, until the acidic hydrolytic fragment is analyzed the above formula is to be taken with reserve. The necine from the hydrolysis with methanolic potassium hydroxide was isolated as the hydrochloride and proved to be identical with retronecine hydrochloride (m.p. and mixed m.p. 164° C.). The author found the melting point of the free base to be 118° C. although the specimen was not as carefully purified as that of Barger *et al.* The acidic fragment, though crystalline, was difficult to purify.

#### *S. mikanioides* (Walp.) Otto

The author is greatly indebted to Dr. D. Aston, Chief Chemist of the Department of Agriculture, Wellington, New Zealand, for supplying this plant. There was available 13.95 kilos which in the fresh condition had weighed 101 kilos. Owing to the pronounced aromatic odor of the extract, it was distilled with steam and the distillate extracted with ether. The residue from the ether extract on fractional distillation yielded a main fraction which solidified partly on cooling. Adhering oil was removed by pressing between hardened filter papers in a press. The thoroughly dry crystals thus obtained

\* All melting points are corrected.



melted sharply at  $64^{\circ}$ . Analytical figures agree with  $(C_5H_8O_2)_n$ . Owing to its comparatively low boiling point  $n$  in this formula is probably 2. Calcd. for  $C_{10}H_{16}O_4$ : C, 60.00; H, 8.00%. Found: C, 59.93; H, 8.02%.

The alkaloid, for which the name *mikanoidine* is proposed, was present only to the extent of 0.02%. Efforts to obtain the free base or a salt crystalline were unsuccessful. The base (3 gm.) was therefore treated with 2 gm. of potassium hydroxide in 50 cc. of methanol. After 24 hr. the solvent was largely evaporated. A little water was added and the remainder of the methanol boiled off. The alkaline solution was then repeatedly extracted with ether and the combined extract dried over potassium carbonate. Removal of the solvent left a pale yellow oily base which did not crystallize in the course of several days. Neither could the hydrochloride be obtained crystalline, and there appeared to be some decomposition in the presence of excess of acid. The picrate, however, crystallized readily from methanol in which it is only moderately soluble. After being recrystallized from the same solvent, it melted sharply at  $186^{\circ}$  C. and the cooled melt rapidly resolidified. This is evidently *mikanecine* picrate and the free base,  $C_8H_{15}O_2N$ , may be a dihydro-retronecine. Calcd. for  $C_8H_{15}O_2N : C_6H_3N_3O_7$ : C, 43.52; H, 4.66; N, 14.51%. Found: C, 43.81; H, 4.62; N, 14.55%.

The alkaline solution from which the *mikanecine* had been extracted was acidified with hydrochloric acid and again exhausted with ether. The combined extract was freed of solvent and the residue recrystallized from hot water in which it is only sparingly soluble. *Mikanecic* acid,  $C_{13}H_{18}O_5$ , as thus obtained melts sharply at  $240^{\circ}$  C. Calcd. for  $C_{13}H_{18}O_5$ : C, 61.90; H, 6.35%; M.W. 252. Found: C, 61.29; H, 6.16%; M.W. 254, 260. *Mikanoidine* is therefore  $C_{21}H_{29}O_6N$ .

#### *S. aureus* L.

This plant was collected in Northern Alberta in June and July 1935. There was available 810 gm. of dry material which yielded 0.05 gm. of alkaloid. It was recrystallized from a large volume of boiling ether in which it is only very sparingly soluble. A second recrystallization from methanol, in which it is only sparingly soluble, yielded the alkaloid, for which the name *aureine* is proposed, in hard stout prisms melting with decomposition at  $238^{\circ}$  C. The decomposed melt gave a pink color with Ehrlich's reagent. Calcd. for  $C_{18}H_{26}O_5N$ : C, 64.48; H, 7.46; N, 4.18%. Found: C, 64.40; H, 7.44; N, 4.47%.

#### *Degradation of Retrorsine Methiodide*

A solution of the methiodide (4.4 gm.) in hot water was treated with silver oxide until no further visible reaction occurred and until a test portion showed the absence of halogen. The filtered solution was evaporated to complete dryness *in vacuo* and the colorless resinous residue heated cautiously over a free flame until some darkening took place. Care was taken to avoid superheating, but at the same time to ensure complete decomposition. Ether extraction at this point did not yield the ester mentioned in the introduction.

The residue was dissolved in chloroform, and in general only a small amount of insoluble material remained. The filtered solution (charcoal) was treated with an excess of methyl iodide. In the course of several days a dark oily precipitate was formed. The solvent was then largely removed and the residue extracted with hot methanol. The filtered solution (charcoal) was evaporated to a small volume and treated with a large volume of dry ether. The insoluble portion (*R*) was again extracted with ether, and the combined extracts evaporated to a small volume. In the course of several days crystallization of the ester was generally complete. Adhering oil was removed by cautious washing with ether. One recrystallization from much dry ether, in which the substance is only moderately soluble, served to yield pure  $\alpha$ -hydroxy-propionaldehyde (?) retronecate in large deep plates melting sharply at 125° C.; Calcd. for  $C_{13}H_{18}O_8$ : C, 57.78; H, 6.67%; M.W. 270. Found: C, 58.08; H, 7.01%; M.W. 270, 276.

Hydrolysis with aqueous potassium hydroxide, acidification, and ether extraction of the resulting solution served to yield pure retronecic acid identical (m. p. 177° C.) with a specimen prepared from the dipotassium salt.

The syrupy residue, from which ether failed to remove any more of the above ester, was treated with an excess of silver oxide in water and the mixture digested on the steam bath. The aqueous filtrate (charcoal) from this mixture was evaporated to a syrup and then evaporated repeatedly with anhydrous methanol. If crystals for seeding are available the betaine (?) may be crystallized at this point. Further purification may be effected by boiling the aqueous solution with dilute hydrochloric acid and decolorizing with charcoal. Removal of the acid by means of silver oxide, evaporation of the filtrate to a syrup and addition of methanol are generally sufficient to induce crystallization. The substance was recrystallized from hot methanol in which it is only sparingly soluble. It is very soluble in water, which solution is neutral to litmus, but insoluble in chloroform and other non-hydrolytic solvents. It melts at 256° C. with some charring; only the decomposed melt gives a red color with Ehrlich's reagent. Calcd. for  $C_8H_{13}O_3N$ : C, 59.01; H, 7.11; N, 7.65%. Found: C, 58.59; H, 7.36; N, 7.91%.

Benzoyl-retronecine when subjected to a parallel procedure yielded the same material.

#### *Hydroxy-acetone Retronecate*

Purified retronecic monolactone (1.07 gm.) was dissolved in acetone and treated with 0.35 gm. of anhydrous potassium carbonate in a small volume of water. The mixture was evaporated to dryness and then heated under reflux with 0.48 gm. of chloroacetone in 100 cc. of dry methanol (90 min.) together with a crystal of potassium iodide. The solvent was distilled off and the residue extracted with ether. The extract was evaporated to a syrup and then extracted with several successive portions of low boiling petroleum ether. Removal of most of the solvent and the addition of ether induced immediate crystallization. The ester was further purified by re-

crystallizing once from boiling ether in which it is only sparingly soluble; it then melted sharply at 137° C. With ammoniacal silver nitrate it gave an immediate deposit of metallic silver. A mixture of this ester with the ester from retronecine melted at once when placed in a bath at 115° C. Calcd. for  $C_{13}H_{18}O_6$ : C, 57.78; H, 6.67%. Found: C, 57.73; H, 6.78.

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## STUDIES ON LIGNIN AND RELATED COMPOUNDS

XX. METHANOL LIGNIN AND ITS RELATION TO THE SO-CALLED  
"PRIMARY LIGNIN" OF FRIEDRICH AND DIWALD<sup>1</sup>BY E. G. KING<sup>2</sup> AND HAROLD HIBBERT<sup>3</sup>

## Abstract

Pretreatment of spruce wood meal with cold 5% sodium hydroxide decreases the amount of lignin extractable with methanol and anhydrous hydrogen chloride (Hibbert-Brauns method). Such a prior treatment of the wood meal, either in an atmosphere of nitrogen or of air, apparently causes no structural change in the lignin as judged by the methoxyl content. The method of Friedrich and Diwald, which involves a preliminary treatment with 17% hydrochloric acid followed by addition of a hot alcohol, represents a much more drastic process than the Hibbert-Brauns method, as is indicated by the darker color, lower methoxyl content and behavior towards 8-10% alkali of the isolated lignin.

Methanol lignin isolated from a resin-free spruce wood meal, previously subjected to treatment with 5% cold alkali in the presence or absence of air, shows no loss of methoxyl groups on treatment with 8-10% alkali; the same is true of the "primary lignin" prepared by the method of Friedrich and Diwald; in both cases the lignin is insoluble in sodium bicarbonate. These facts show that neither methanol lignin nor "native lignin" contains ester methoxyl groups, as assumed by Friedrich and Diwald. Prolonged treatment of methanol lignin with alkali in the presence of air, especially at higher temperatures, apparently brings about certain changes in its structure, including possibly the formation of carboxyl groups. The claim of Friedrich and Diwald that their product represents an "unchanged native lignin" is not in accordance with the facts, and their assumption of the presence of carboxyl groups in native lignin is incorrect.

## Introduction

Previous work on methanol lignin (1) would seem to show that it has undergone minimum alteration in structure during its isolation. In view of Friedrich and Diwald's (4) rather broad claims for their material as true "native lignin", and the more drastic method of extraction, it seemed advisable to repeat their work.

The mode of pretreatment of the wood prior to extraction involves removal of resins alone in some cases and of both resins and gummy substances in others (5, 6, 7, 8, 12, 13, 14).

The removal of resins prior to the lignin extraction is imperative, since they can be removed only with the greatest difficulty when present in the isolated lignin. On the other hand, the desirability of a prior extraction of the pentosans and hemicelluloses is a debatable point. Friedrich and Diwald (4) claim that the quantitative removal of gummy substances is essential to a satisfactory isolation of a lignin suitable for scientific investigation, and that thereby larger yields of so-called "primary lignin" are obtained.

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To determine whether a similar treatment would increase the yield in the case of methanol lignin, resin-free spruce meal was treated with aqueous 5% sodium hydroxide at room temperature in an atmosphere of nitrogen, and the methanol lignin then extracted by the Brauns-Hibbert method (1).

As shown in Table I the amount of lignin isolated corresponds with that actually removed from the wood. The amount of lignin obtained from resin-free spruce wood, which has not been previously subjected to an alkali treatment, is of the order of 8%, calculated on the dry weight of the original wood meal, as compared with 6.5% when an alkali-pretreated wood is used. A similar result has been obtained by Harris (6).

In a more recent contribution, Friedrich and Bruda (3) conclude that acid hydrolysis of the wood meal prior to the extraction with alcohol is not an essential factor, although it increases the quantity of lignin extracted.

To clarify this point, "primary lignin" (Friedrich and Diwald) was extracted from a sample of an alkali-pretreated wood meal by means of a prior treatment with 17% hydrochloric acid followed by an extraction with ethyl alcohol. It was found to possess properties different from those claimed by Friedrich and Diwald (Table II). Also, the methanol lignin extracted from a resin-free wood meal, previously extracted with cold 5% alkali in an atmosphere of nitrogen, appears to be identical with that prepared from a resin-free but non-alkali-extracted wood meal.

#### *Effect of Variation in Conditions of Alkali Pretreatment*

Spruce wood meal subjected to an alkali pretreatment *in the presence of air* yielded a lignin identical with ordinary methanol lignin, as shown by methoxyl content, color and solubility.

Friedrich and Diwald (4) state: "In one instance, where the preparation of 'primary lignin' was preceded by an extraction of the wood meal with warm alkali, the lignin isolated had a methoxyl content of only 16.7%". This experiment was repeated twice, the wood meal being pretreated in each case with 5% sodium hydroxide at 65° C. for 32 hr. in an atmosphere of nitrogen, and the lignin isolated, using absolute methyl alcohol and hydrochloric acid, but no lowering in the methoxyl content of the isolated lignin was observed (Table II).

The methoxyl content of the methanol lignin prepared from spruce meal previously subjected to varying alkaline treatment is seen not to vary markedly from that of methanol lignin ( $\text{OCH}_3$ , 21.7–23.0%) prepared from a non-alkali-extracted wood meal. The methoxyl value of the "primary lignin" is lower than that of the methanol lignin, indicating the more drastic nature of the Friedrich and Diwald method of isolation.

Methanol lignin extracted from alkali-pretreated wood meal was completely soluble in 1% sodium hydroxide but only partially soluble in 8–10%. When separated by the latter treatment, the soluble methanol lignin fraction was found to have a methoxyl content of 21.6%, and the insoluble portion, 23.1%. That the behavior of this lignin is not the result of the previous

TABLE II  
PRETREATMENT OF WOOD MEAL WITH ALKALI IN RELATION TO YIELD AND METHOXYL  
CONTENTS OF LIGNIN ISOLATED

| Pretreatment of spruce wood meal extracted with alcohol-benzene and water      | Method of lignin extraction             | Yield calculated on original alkali-extracted bone-dry wood meal, % | Methoxyl of lignin isolated, % |
|--|---|---|--------------------------------|
| (a) Extracted with 5% NaOH in atmosphere of nitrogen                           | (1) Methanol lignin (autoclave)         | 4.13  | 21.7                           |
|  | (2) "Primary lignin" (F. and D. method) | 7.2   | 20.1                           |
| (b) Material from (a) extracted with 5% NaOH at 65° C., atmosphere of nitrogen | (3) Methanol lignin (bomb tube)         | 5.0   | 23.2                           |
| (c) Extracted with 5% NaOH in oxidizing atmosphere (air)                       | (4) Methanol lignin (bomb tube)         | 6.0   | 22.4                           |
|  | (5) "Primary lignin" (F. and D. method) | —   | 19.1                           |

alkaline treatment was shown by the similar behavior of methanol lignin extracted from wood meal not pretreated with alkali.

It has also been found that all methanol lignins containing more than 21% methoxyl may be separated by solution in dioxane and precipitation with dry ether into two fractions: a principal ether-insoluble fraction, and, in much smaller yield (15–20%), an ether-dioxane-soluble fraction with a methoxyl content considerably greater than 23%. The fractionation of methanol lignin will be discussed in more detail in a further communication (2).

According to Friedrich and Diwald, the methoxyl content of their "primary lignin" decreases from 20.9 to 12.7% on warming gently with 2*N* sodium hydroxide, the resulting product now being soluble in sodium carbonate solution. They conclude that of the five methoxyl groups in the molecule, two are attached as "ester-", the remaining three as "ether-linkages". In a later paper Friedrich (4a) has modified this conception, claiming the presence of only one ester methoxyl group in "primary lignin". The incorrectness of these views is indicated by the results shown in Table III.

TABLE III  
ACTION OF ALKALI ON METHANOL LIGNINS AND "PRIMARY LIGNIN" IN RELATION TO  
PERCENTAGE METHOXYL CONTENT

| Product              | Methoxyl value of original product | Methoxyl values after specified treatment |  |   |  |
|----------------------|------------------------------------|---|--|---|--|
|                      |                                    | 2 <i>N</i> alkali at 50° C. for 2 hr.     | 2 <i>N</i> alkali at 100° C. for 2 hr. | 0.25 <i>N</i> alkali in oxidizing atmos. for 12 hr. at room temp. | 0.25 <i>N</i> alkali in oxidizing atmos. for 12 hr. at 100° C. |
| Methanol lignin (1)* | 21.7                               | 21.6                                      | 21.5                                   | 20.6**  | 18.6**   |
| Methanol lignin (3)  | 23.2                               |   |  |   |  |
| Methanol lignin (4)  | 22.4                               | 21.9                                      |  |   |  |
| "Primary lignin" (2) | 20.1                               | 19.6                                      |  |   |  |
| "Primary lignin" (5) | 19.1                               | 18.6                                      |  |   |  |

\*Numbers refer to products described in Table II.

\*\*The authors acknowledge their indebtedness to G. H. Tomlinson, Jr., for these experimental results.



No appreciable decrease in methoxyl content takes place under the influence of alkali (Table III), proving definitely that neither methanol lignin nor "native lignin" contains ester methoxyl groups. The slight decrease in methoxyl content suffered by "primary lignin", in contrast with the stability of the methanol lignin, indicates that certain structural changes are brought about in the former under the influence of hydrochloric acid (17%).

The pronounced change in methoxyl content (Table III, last column) shows that, under the influence of a higher temperature and an oxidizing atmosphere (air), a marked alteration in properties has occurred, and this is further indicated by the fact that the resulting product is carboxylic in nature, being soluble in sodium bicarbonate solution. It is possible that the formation of the carboxyl group may be due to the presence in the lignin of a pyrone or furane ring, as first proposed by Klason (9) and later by Rassow (11). Since neither the methanol lignin nor the "primary lignin" employed in the present investigation was found to contain ester methoxyl groups, the carboxyl groups present in Friedrich and Diwald "primary lignin" (4) were presumably formed in this manner.

### Experimental

#### *Preliminary Treatment of the Spruce Wood Meal*

Spruce wood meal (100 mesh, 500 gm.) was extracted with alcohol-benzene (1 : 1), then with water and dried in the vacuum oven at 60° C. This material (425 gm.) was stirred at room temperature in a large bottle with 12.5 litres of 5% sodium hydroxide (625 gm.) for 38 hr. in an atmosphere of nitrogen, allowed to settle for four hours, and the liquor syphoned off. This treatment was repeated four times. The residual wood meal was washed well with water by decantation (12 litres for each washing), then stirred with four litres of 1% acetic acid to neutralize any remaining alkali, filtered and washed on a Büchner-funnel until free from acid. It was stirred with six litres of hot water, filtered and pressed in a hydraulic press, air-dried for a few hours, mixed with two litres of methyl alcohol, again filtered, air-dried, and finally dried at 60° C. (16–20 mm.) for 40 hr. Yield, 317 gm.

#### *Isolation of Methanol Lignin*

Dry, alkali-extracted wood meal (240 gm.) was placed in a glass-enamel-lined autoclave with two litres of absolute methyl alcohol containing 40 gm. of dry hydrogen chloride (2%), and the mixture heated with stirring at 75–78° C. under pressure for five days. The reaction mixture was filtered, washed with methyl alcohol and dried, the residual solid material returned to the autoclave, and the same quantity of methanol-hydrogen chloride added. Three complete extractions were made.

The combined filtrates were first evaporated under reduced pressure to about 100 cc., centrifuged and filtered through a sintered glass funnel, and then poured in a fine stream, with stirring, into about three litres of distilled water to which a little potassium bicarbonate had been added. The brown flocculent product was filtered, washed with distilled water, and dried.

The material was dissolved in dioxane to give approximately a 15% solution, centrifuged, filtered, and the filtrate added dropwise, with vigorous stirring, to six times its volume of dry ether. The ether was decanted off from the light-brown flocculent precipitate and the residue washed twice with fresh ether, once with petroleum ether, and dried. The product from the first extraction was buff colored and very finely divided, while that from the second and third extraction was slightly darker in color. The results are shown in Tables I and IV.

TABLE I  
ANALYTICAL DATA OF EXTRACTED PRODUCTS (SEE TABLE IV)

| Method of successive treatment of wood meal     | % Lignin* remaining in wood meal after each successive treatment |  | % Methoxyl** of lignin isolated |
|---|--|--|---------------------------------|
|   | (i) Calcd. on basis of residue obtained                          | (ii) Calcd. on basis of alkali-extracted wood meal |                                 |
| Alcohol-benzene and water                       | 28.1   | —  | —                               |
| 5% alkali                                       | 30.3   | 30.3   | —                               |
| CH <sub>3</sub> OH + 2% HCl (75–78° C.)         |  |  |                                 |
| 1st extraction                                  | 34.5   | 27.3   | 21.7                            |
| 2nd extraction                                  | —  | —  | 19.4                            |
| 3rd extraction                                  | 36.0   | 23.8   | 18.7                            |
| % lignin lost in extraction = 30.3 – 23.8 = 6.5 |  |  |                                 |
| % lignin isolated = 6.4                         |  |  |                                 |

\*Lignin was determined according to the modified Ross-Potter method (10).

\*\*Methoxyl determinations were carried out by the Zeisel method.

TABLE IV  
LIGNIN EXTRACTION OF ALKALI-PRETREATED SPRUCE MEAL WITH ABSOLUTE METHYL ALCOHOL AND 2% HYDROGEN CHLORIDE

| Description  | Dry wt. after extraction, gm. | Loss in wt., gm. | % loss, on original wood meal | Wt. of purified methanol lignin isolated, gm. | % Lignin extracted on basis of original wood meal |
|--|-------------------------------|------------------|-------------------------------|---|---|
| Original wood meal (extracted with alcohol-benzene, water and alkali (5%)) | (240)                         | —                | —                             | —   | —   |
| 1st extraction with methanol-HCl   | 190                           | 50               | 20.8                          | 9.33  | 3.89  |
| 2nd extraction with methanol-HCl   | —                             | —                | —                             | 3.95  | 1.64  |
| 3rd extraction with methanol-HCl   | 160                           | 30               | 12.5                          | 1.54  | 0.64  |
| Total ether-soluble fractions from 1st, 2nd and 3rd extractions            | —                             | —                | —                             | 0.61  | 0.25  |
| Total  |                               | 80               | 33.3                          | 15.43   | 6.42  |
| Cold alkali-extracted spruce wood meal extracted with alkali at 65° C.     | 12.4                          | 3                | 19.5                          | 0.77  | 5.0   |

*Isolation of "Primary Lignin" (Friedrich and Diwald Method)*

Dry, alkali-extracted spruce wood meal (11.6 gm.) prepared as above was allowed to stand for 48 hr. at room temperature with 45 cc. of 17% hydrochloric acid, and the mixture then refluxed for 24 hr. with 450 cc. of 95% ethyl alcohol. After the solution had been filtered, and the filtrate concentrated and added dropwise to water, a light-brown product was precipitated. This became darker on drying. (Loss of wood meal, 30%.) The product was purified by solution in dioxane and precipitation in ether. Yield 0.83 gm., or 7.2%. Found:  $\text{OCH}_3$ , 20.1%.

*Effect of Pretreatment of Wood Meal with Alkali at 60–65° C.*

Wood meal (50 gm.) previously extracted with benzene-alcohol, followed by water, was treated for nine hours in an atmosphere of nitrogen with one litre of 5% sodium hydroxide at 60–65° C. The alkaline solution was much darker in color than that obtained when the extraction was carried out at room temperature. On acidifying a sample of the filtered solution, only a small white precipitate was obtained, indicating that nearly all the gums and hemicelluloses had been extracted in the previous treatments. The product was filtered, washed with water, acetic acid, hot water and dried as before.

The extracted meal was then heated for five days at 78° C. in a sealed bomb tube with ten times its weight of absolute methyl alcohol containing 2% anhydrous hydrogen chloride. The lignin was isolated and purified as described previously. Found:  $\text{OCH}_3$ , 23.0%.

A second similar experiment was carried out with the quantities shown in Table IV, in which the yields are also given. Found:  $\text{OCH}_3$ , 23.2%.

*Effect of Pretreatment of Wood Meal with Alkali in an Oxidizing Atmosphere*

Resin-free wood meal (100 gm.) was stirred in a large flask with five litres of 5% sodium hydroxide at room temperature for 36 hr., during which time air was bubbled through the mixture. The liquor was syphoned off and this treatment repeated three times. During this process the wood meal became orange-colored, and the liquors, dark brown. No odor of vanillin, as described by Friedrich and Diwald, was detectable either during the extraction or on acidification of the liquors. The residual wood meal was washed with acetic acid (1%), then with water and dried in the vacuum oven at 60° C. The yield of light-yellow meal was 78 gm.

Methanol lignin and "primary lignin" were then prepared from this material as previously described (Table II).

*Fractionation of Methanol Lignin by Use of Sodium Hydroxide (8–10%)*

Methanol lignin ( $\text{OCH}_3$ , 21.7%, see Table I) (1 gm.) was warmed slightly (50° C.) for two hours with 50 cc. of 8–10% sodium hydroxide, and then filtered through a sintered glass funnel. The soluble lignin fraction was isolated by adding the filtrate dropwise to cold hydrochloric acid (1%),

filtering, washing, drying, and finally purifying by solution in dioxane and precipitation with ether. Yield, 0.86 gm. The insoluble lignin fraction was washed with acetic acid (1%), then with water, dried, dissolved in dioxane and reprecipitated with ether. Yield, 0.14 gm. This fractionation by means of alkali is possible only when the alkali concentration is not less than 8–10%, owing to the complete solubility of the lignin in solutions of lower alkali concentrations. Found:— Alkali soluble:  $\text{OCH}_3$ , 21.5%; Alkali insoluble:  $\text{OCH}_3$ , 23.2%.

Each of the fractions differed from the product described by Friedrich and Diwald in that neither was soluble in sodium bicarbonate solution nor underwent any appreciable decrease in methoxyl content during the treatment described above.

#### *Action of Alkali (8–10%) on Methanol- and "Primary" Lignins*

The following experiments show the behavior towards alkali (8–10%) of each of two types of lignin, prepared from wood meals pretreated with alkali (5%) under non-oxidizing and oxidizing conditions respectively.

#### *Experiment A*

In this experiment the methanol lignin and "primary lignin" were extracted from wood meal treated previously with 5% sodium hydroxide in an atmosphere of nitrogen.

(I) *Methanol lignin*: Methanol lignin ( $\text{OCH}_3$ , 21.7%) was heated with 8–10% alkali at 100° C. for two hours, the methoxyl content again remaining practically unchanged. Found:  $\text{OCH}_3$ , 21.5%.

(II) *"Primary lignin"* (Friedrich and Diwald method): After heating 0.5 gm. of "primary lignin" ( $\text{OCH}_3$ , 20.1%) with 20 cc. of 8–10% alkali at 50° C. for two hours, the lignin was isolated and purified. Found:  $\text{OCH}_3$ , 19.1%.

#### *Experiment B*

In contrast with the products employed in Experiment A, the methanol lignin and the "primary lignin" used in this experiment were extracted from wood meal previously treated with 5% sodium hydroxide in an oxidizing atmosphere.

(I) *Methanol lignin*: Methanol lignin ( $\text{OCH}_3$ , 22.4%, 0.5 gm.) was heated with 15 cc. of 8–10% sodium hydroxide for two hours at 50° C. The recovered and purified lignin was light brown and was insoluble in sodium bicarbonate solution. Yield, 0.39 gm. Found:  $\text{OCH}_3$ , 21.8%.

(II) *"Primary lignin"* (Friedrich and Diwald method): "Primary lignin" ( $\text{OCH}_3$ , 19.1%) was treated in the same manner and the product purified with dioxane-ether. The dark brown lignin product was also insoluble in sodium bicarbonate. Found:  $\text{OCH}_3$ , 18.6%.

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## THE HYDRATION OF DICALCIUM SILICATE AND TRICALCIUM SILICATE<sup>1</sup>

BY N. B. KEEVIL<sup>2</sup> AND T. THORVALDSON<sup>3</sup>

### Abstract

Samples of  $\beta$ -dicalcium silicate,  $\gamma$ -dicalcium silicate, tricalcium silicate, hillebrandite and dehydrated hillebrandite were exposed to saturated steam at temperatures between 50° and 375° C. After drying to constant weight (usually over calcium oxide) the increase in weight and the amount of free calcium hydroxide were determined. Microscopic examinations and X-ray diffraction patterns of the products were made. The hydration products were then dehydrated and similar studies of the products made. The hydrolysis of the hydration products also was studied.

It was found that between 110° and 350° C.  $\beta$ - and  $\gamma$ -dicalcium silicates may absorb water without hydrolysis to form three crystalline products. Two of these are identical with products already described (20); the third product appears to possess another characteristic crystalline structure as shown by the X-ray pattern, but to have a variable water content with a limiting composition of  $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ . The hydration product may be dehydrated without the liberation of lime.

When conditions favoring hydrolyses are avoided, tricalcium silicate hydrates directly to a crystalline hydrate which probably has the limiting composition,  $3\text{CaO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , although products holding from 1.3 to 2 moles of water give the same X-ray diffraction pattern. When the conditions favor partial hydrolysis, tricalcium silicate decomposes into calcium hydroxide and crystalline hydrated dicalcium silicate. Dehydration of hydrated tricalcium silicate gives one mole of lime along with dicalcium silicate.

Hillebrandite exposed to saturated steam at 160° C. remained unchanged, while a sample of dehydrated hillebrandite on hydration gave a product similar to that obtained from  $\beta$ -dicalcium silicate.

When treated with a large excess of water, the hydrated silicates hydrolyze to the same extent as the anhydrous silicates, but the final equilibrium is attained more rapidly, especially in the case of hydrated dicalcium silicate.

### Introduction

The physical and chemical changes that occur during the setting and hardening of Portland cement have been the subject of many experimental studies. Some of these studies have dealt with commercial cements, others with the compounds considered to be present in Portland cement clinker. The investigations on the hydration and hydrolysis of the compounds considered to be present in Portland cement clinker may be divided into two groups, one dealing with the silicates of calcium, the other, with the compounds containing alumina and ferric oxide. The present paper will deal only with the two silicates of calcium which normally form about 75% of Portland cement clinker.

Considering more particularly the investigations of Le Chatelier (9), Michaëlis (11), Newberry and Smith (14), Bates and Klein (1), Lerch and Bogue (10), Thorvaldson and Vigfusson (18), and Kühl and Mann (8), the conclusion is reached that when tricalcium silicate and dicalcium silicate are

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exposed to water, lime is liberated with the ultimate formation of a gelatinous calcium hydrosilicate, the composition of which depends on the final concentration of calcium hydroxide in the liquid phase. The composition of the solid or gelatinous phase may vary from hydrated silica, when the final concentration of lime in the liquid phase is very low, to a material with a molar ratio of lime to silica of 3 : 2, when the liquid phase at equilibrium is just saturated with calcium hydroxide. Solutions highly supersaturated with respect to calcium hydroxide may be obtained when tricalcium silicate is shaken with still smaller quantities of water, and possibly the lime-silica ratio of 3 : 2 for the solid phase may be exceeded under these conditions.

There is a considerable divergence of opinion concerning the quantitative interpretation of the observed experimental results in terms of the chemical compounds formed. Le Chatelier (9) considered that the only chemically distinct hydrated calcium silicate that can exist in the presence of water containing calcium hydroxide has the composition  $\text{CaO} \cdot \text{SiO}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , and that when the hydrated product contains more calcium oxide than this, the "excess of lime is fixed in some other way than in the state of definite combination." Michaëlis (11) concluded that the hydration product is a hydrosilicate gel of variable composition which cannot be considered in terms of chemical combination. Most experimenters are, however, agreed that a definite compound of the composition  $\text{CaO} \cdot \text{SiO}_2 \cdot x\text{H}_2\text{O}$  probably exists. Strong experimental support is given by the sharp turn at the 1 : 1 ratio in the curve obtained by plotting the ratio of lime to silica in the gel at equilibrium against the original weight of the silicate treated with a fixed volume of water, as found by Thorvaldson and Vigfusson (18) for both tricalcium and dicalcium silicate. This has been confirmed by Kühl and Mann (8). A large number of determinations of the loss on ignition of the product  $\text{CaO} \cdot \text{SiO}_2 \cdot x\text{H}_2\text{O}$ , formed by the hydrolysis of tricalcium silicate, indicated that the composition of this product after drying to constant weight over quicklime is represented by  $\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ .\* This does not preclude the possibility of the existence of a higher hydrate when the gel is in equilibrium with the solution, or with a drying agent having higher aqueous tension than the system calcium oxide-calcium-hydroxide. According to Koyanagi's (7) results, the hydrate contains two moles of water.

These investigations disclose very little as to the nature of the gel phase in equilibrium with solutions having final concentrations of calcium hydroxide above or below that required for the formation of the monocalcium silicate. The ratio of lime to silica in the gel at equilibrium appears to increase continuously with the dissolved lime until the system is saturated with calcium hydroxide. This suggests that the water may remove the lime from the silicate in a zeolitic manner and that, with reference to phase rule equilibria, the gel phase may be analogous to a solution. The experimental results are not in disagreement with the assumption that a hydrate of the composition

\* Unpublished determinations by J. L. Binder in this laboratory.

$3\text{CaO} \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$  is formed when the liquid phase is saturated with calcium hydroxide under conditions of equilibrium. However, in the absence of definite evidence of a break in the curve for the change in lime-silica ratio with the equilibrium concentration of dissolved lime, the main reason for this assumption is the natural occurrence of such a compound in well crystallized form (afwillite,  $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ ). Kühl and Mann (8) consider that a series of hydrated calcium silicates exist having lime-silica ratios from 1 : 1 as the lower limit to 2 : 1 as the probable upper limit in supersaturated solutions of lime.

Flint and Wells (4) recently published a report of a very extensive investigation on the system calcium oxide-silica-water at  $30^\circ \text{C}$ ., including the reaction of water on the anhydrous calcium silicates. They consider that when  $\beta$ -dicalcium silicate and  $\gamma$ -dicalcium silicate are exposed to water, hydrolysis at first takes place with the formation of a solution of  $\text{CaH}_2\text{SiO}_4$  together with increasing amounts of  $\text{Ca}_3(\text{HSiO}_4)_2$  as the lime concentration in the solution increases, and that the composition of the hydrated material finally precipitating out, as the concentration of lime reaches saturation or supersaturation, approaches that of hydrated dicalcium silicate. They consider that the reaction of water with tricalcium silicate is essentially similar, except that the liberation of free lime and the attainment of saturation are much more rapid, and the tendency for supersaturation to occur much greater than with the 2 : 1 compound. They also report "that well-defined crystalline dicalcium silicate is formed by reaction between tricalcium silicate and water at  $150^\circ \text{C}$ . and crystalline calcium hydroxide."

Nacken (12), studying the action of water on tricalcium silicate, reports the formation of hydrosilicates of the formula  $2\text{CaO} \cdot \text{SiO}_2 \cdot x\text{H}_2\text{O}$ ,  $3\text{CaO} \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$ , and  $\text{CaO} \cdot \text{SiO}_2 \cdot x\text{H}_2\text{O}$ .

Bogue and Lerch (2), who gaged tricalcium silicate and dicalcium silicate with small quantities of water, suggest that these silicates form a hydrosilicate with a lime-silica ratio of 2 : 1.

There is no evidence that any of the hydrosilicates produced by hydration of the silicates of calcium at room temperature, as described above, are crystalline. Thus, X-ray diffraction patterns of the products have never been obtained. This is peculiar considering the fact that well defined crystalline substances analogous to most of these products occur naturally (19), and suggests that the gel systems formed are in some way analogous to solutions in a metastable state. Crystalline calcium hydrosilicates have also been obtained by hydrothermal synthesis from lime and silica in saturated steam at temperatures higher than  $100^\circ \text{C}$ . Reference is especially made to the extensive work of Nagai (13) who reports the formation of  $\text{CaO} \cdot \text{SiO}_2 \cdot 1/4\text{H}_2\text{O}$ ,  $3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ ,  $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 8\text{H}_2\text{O}$  and  $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ ; and to that of Thorvaldson and Shelton (17) and of Vigfusson, Bates and Thorvaldson (20) who prepared, and made optical and X-ray studies of, two crystalline products of the composition  $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ .

The authors are not aware of any reports of the direct hydration of tricalcium silicate or dicalcium silicate to form well defined crystalline products without hydrolysis, except that of Thorvaldson (15, 16) which referred to the work described in the present paper. The hydrated dicalcium silicate described by Thorvaldson and Shelton (17) was probably formed simultaneously by the hydrolysis of the tricalcium silicate of the Portland cement used, by the reaction between the free calcium hydroxide liberated and the silica sand and by the direct hydration of the  $\beta$ -dicalcium silicate of the cement. The "well-defined crystalline dicalcium silicate" reported by Flint and Wells (4) was formed by hydrolysis of tricalcium silicate at 150° C.

### Experimental

#### *Materials and Experimental Procedure*

The method of preparation of the silicates of calcium has been described elsewhere (5, 6). The samples contained no free lime, a minute trace of iron and a small quantity of magnesia. The tricalcium silicate contained about 2% of tricalcium aluminate, and the dicalcium silicate contained about an equivalent quantity of alumina, probably as monocalcium aluminate. The samples of tricalcium silicate contained some  $\beta$ -dicalcium silicate and the dicalcium silicates contained a small quantity of monocalcium silicate.

The silicates, ground to pass 200 mesh, were weighed into platinum crucibles and these, protected from condensing water, were exposed to saturated steam at temperatures varying from 50° to 375° C. After removal of the samples from the autoclave, the products were dried, unless otherwise stated, in a vacuum over calcium oxide until constant in weight. Sometimes the silicate was moistened with a saturated solution of calcium hydroxide before treatment in the autoclave. Care was taken to avoid contamination with carbon dioxide. Samples of pure lime exposed with the silicate samples in the autoclave and desiccator were found to be entirely free from carbonate at the end of the experiment.

In calculating the water taken up by the silicates, corrections for the water held by the impurities as determined by blank tests with these substances under similar conditions were applied. The uncertainties due to impurities were thus largely eliminated. Free lime was determined by the method of Emley, as modified by Lerch and Bogue. Since the free lime was present as the hydroxide, long periods of digestion were necessary.\*

The refractive indices were determined in the usual way by means of a petrographic microscope, using sodium light. The exact refractive indices of the immersion liquids were determined with a Pulfrich refractometer. Photographs of the X-ray diffraction patterns of the powdered hydrates were made with a General Electric Company multiple spectrograph. A Coolidge tube with a molybdenum target was the source of the X-rays, and a zirconia filter was used.

\* Titration with bromthymol blue to a green color was found to give satisfactory results.

## I. EXPERIMENTS WITH DICALCIUM SILICATE

*The Products of Hydration*

Experiments were made with both  $\beta$ - and  $\gamma$ -dicalcium silicates, exposing these to saturated steam at temperatures of 110° to 350° C. Absorption of water took place without appreciable hydrolysis except at 110° C. At this temperature a small amount of free lime was present at times in the hydrated material (less than 0.1 mole of free lime per mole of dicalcium silicate). Wetting the anhydrous silicate with saturated lime water before the treatment increased the rate of hydration, but the rate often varied in the case of duplicate samples treated side by side in the autoclave. There was no marked difference in the action of the steam on the two crystalline modifications of the silicate.

At 110°–170° C. the maximum hydration was usually reached in about two weeks, the composition of the product, after drying over calcium oxide, corresponding to the formula  $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ . At higher temperatures the absorption of water was much slower. Thus at 220° C. from 0.2 to 0.6 moles were usually held after two weeks' treatment, although the maximum of one mole was occasionally attained, while at 350° C. the amount of water taken up in two days varied from 0.2 to 0.3 moles per mole of dicalcium silicate with an extremely slow increase on further treatment. The appearance of the hydrated material under the microscope suggested that the low absorption of water at the higher temperatures was due possibly to the formation around the grains of the anhydrous silicate of a protective crust that hindered further penetration of water.

The microscopic examination indicated that these hydration products of dicalcium silicate may contain three different types of crystalline material. Mixtures of two of these forms were often found in one sample, but usually one of the crystalline forms predominated. Samples that were entirely or nearly uniform, as shown by microscopic examination, were selected for making X-ray diffraction patterns.

The most common product appeared as very small irregular grains and composite masses of finely crystalline anisotropic material of medium to low birefringence. This material appeared to be responsible for the slowing-up of the rate of hydration, especially at the higher temperatures, and was at first thought to be a hydrate with less than one mole of water per mole of dicalcium silicate. Further it appeared that its refractive index varied with the temperature of the autoclave from a minimum value of less than 1.62, for the material obtained at the lower temperatures, to 1.64 for that obtained at 350° C. As stated above, the samples prepared at the higher temperatures appeared to have unhydrated centres.

Five separate X-ray diffraction patterns were made with this fine-grained material prepared at 170° to 350° C. The water content of these samples varied from 1.0 to 0.3 moles of water per mole of dicalcium silicate, and the mean refractive index from 1.62 to 1.64. Visual comparison of the five patterns indicated that they were all very nearly identical, both as to the lines present and their relative intensities. Thus the amount of water in excess

of a certain small quantity does not seem to alter the crystalline structure materially. This pattern was not similar to that for hillebrandite nor that of any other known hydrate of the composition  $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ , nor of any of the unhydrated silicates of calcium. The readings of the pattern and the relative intensities are given in Table I and in Fig. 1-A.

TABLE I  
X-RAY DATA

The most distinctive of the three crystalline products found in the steam-treated dicalcium silicate exists as well developed plate-like orthorhombic crystals. The optical properties and X-ray diffraction pattern checked exactly with those of the calcium hydrosilicate described by Thorvaldson and Shelton (17), and by Vigfusson, Bates and Thorvaldson (20). When these crystals, instead of the fine-grained material described above, were formed, the hydration to one mole of water per mole of the dicalcium silicate usually occurred fairly rapidly. These crystals apparently form most readily at  $150^\circ\text{--}170^\circ\text{C}$ ., but were sometimes present, appearing etched or poorly developed, at  $220^\circ$  to  $350^\circ\text{C}$ . An almost pure sample was obtained by seeding an unhydrated sample of  $\beta$ -dicalcium silicate with some of these crystals before steam treatment at  $170^\circ\text{C}$ . The amount of water held by this sample after drying to constant weight over calcium oxide agreed with the formula  $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ . There was no free lime present. The refractive indices were  $\alpha = 1.610 \pm 0.002$  and  $\gamma = 1.633 \pm 0.002$ . The readings of the X-ray pattern and a diagram of the pattern in a previous paper may be consulted (20). A diagram is given in Fig. 1-B.

The third crystalline form found in the hydrated samples of dicalcium silicate consisted of small needle-like crystals, possessing a low birefringence and a mean refractive index of  $1.598 \pm 0.003$ . These were never obtained as homogeneous preparations by the direct hydration of dicalcium silicate, but were thus obtained by the steam treatment of 2 : 1 mixtures of lime and silica gel at  $160^\circ$  and  $220^\circ\text{C}$ . There was only 0.65% of free lime present in the preparation obtained on heating at  $220^\circ\text{C}$ . after two weeks' treatment, and the ignition of the material after drying to constant weight over lime indicated the composition  $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ . The refractive index and the

| Fine-grained hydrated dicalcium silicate (average of four patterns) |                              | Hydrated tricalcium silicate (average of five patterns) |                              |
|---|------------------------------|---|------------------------------|
| Planar spacing $d_{hkl}$ in Å                                       | Estimated relative intensity | Planar spacing $d_{hkl}$ in Å                           | Estimated relative intensity |
| 3.03  | SS                           | 3.27  | S                            |
| 2.83  | S                            | 2.99  | SS                           |
| 2.69  | S                            | 2.90  | SS                           |
| 2.49  | S                            | 2.83  | SS                           |
| 2.33  | W                            | 2.60  | M                            |
|   |                              |   | (Variable)                   |
| 1.903   | SS                           | 2.45  | S                            |
| 1.795   | S                            | 2.16  | M                            |
| 1.728   | WW                           | 2.07  | S                            |
| 1.668   | M                            | 1.988   | M                            |
| 1.660   | WW                           | 1.905   | M                            |
|   |                              |   | (Variable)                   |
| 1.547   | M                            | 1.868   | S                            |
| 1.440   | W                            | 1.752   | S                            |
| 1.350   | WW                           | 1.684   | S                            |
| 1.265   | M                            | 1.618   | W                            |
| 1.168   | S                            | 1.560   | S                            |
| 1.042   | WW                           | 1.428   | M                            |
| 1.011   | WW                           | 1.360   | W                            |
| 0.978   | WW                           | 1.235   | W                            |
|   |                              | 1.199   | M                            |
|   |                              | 1.142   | W                            |

Estimated relative intensity: SS = very strong;  
S = strong; M = medium; W = weak;  
WW = very weak



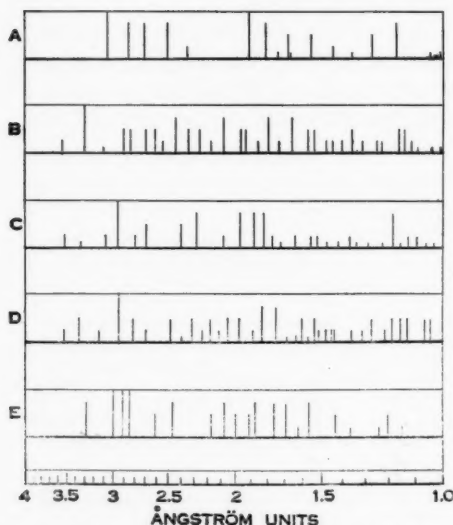


FIG. 1. Diagrammatic representation of X-ray patterns. A. Finely crystalline hydrated dicalcium silicate with water of hydration varying from 0.3 to 1 mole. B. Orthorhombic plates of composition  $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$  (as described by Vigfusson, Bates and Thorvaldson). C. Fine needle-like prisms of composition  $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ . (Similar to those described by Vigfusson, Bates and Thorvaldson.) D. Natural hillebrandite. E. Hydrated tricalcium silicate containing from 1.3 to 1.9 moles water of hydration.

above those for  $\gamma$ -dicalcium silicate. The birefringence of the dehydrated material was also lower. The X-ray diffraction patterns of both these ignited materials were identical, and agreed with that of  $\beta$ -dicalcium silicate. It is possible that the inclusion of air in the crystals is responsible for the low refractive index of these products.

The experiments described above suggest a simple method for preparing pure  $\beta$ -dicalcium silicate which avoids the use of high temperatures and the attendant difficulties with contamination during heat treatments. Pure lime and silica gel in a 2 : 1 ratio, contained in platinum vessels, can be made to combine by treatment in saturated steam in the autoclave at  $220^\circ \text{C}$ ., followed by an ignition at  $900^\circ \text{C}$ . The finely divided form of the final product appears to prevent the inversion of the  $\beta$ - to the  $\gamma$ -form. Samples of  $\beta$ -dicalcium silicate prepared in this way by ignition at  $1000^\circ \text{C}$ . did not show any reversion to the  $\gamma$ -form after storing in sealed glass tubes at room temperature for nearly three years.

#### *Experiments with Hillebrandite*

A specially selected, pure sample of hillebrandite, the naturally occurring mineral of the composition  $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ , was ground to pass 200 mesh.

X-ray pattern showed this material to be identical with the needle-crystals described by Vigfusson, Bates and Thorvaldson (20). A diagram of the pattern is given in Fig. 1-C.

#### *The Dehydration of Hydrated Dicalcium Silicate*

Samples of dicalcium silicate hydrated at  $200^\circ \text{C}$ . to form the fine-grained crystalline material first described above were ignited to constant weight at  $900^\circ \text{C}$ . No lime was liberated. The mean refractive index of the ignited product was  $1.692 \pm 0.005$ . A sample of the prismatic crystals prepared from lime and silica at  $220^\circ \text{C}$ . (refractive index,  $1.598 \pm 0.003$ ) was ignited similarly. The needle form of the particles was retained after ignition (refractive index of ignited material  $1.693 \pm 0.004$ ). These indices were considerably lower than the lower index for  $\beta$ -dicalcium silicate, but well



exposed to saturated steam in an autoclave at 160° C. for eleven days, and then dried over calcium oxide. There was no change in the weights of the samples, and the X-ray patterns of the original hillebrandite and the material after treatment were virtually identical. A diagram of the pattern is given in Fig. 1-D.

When the original hillebrandite was ignited to constant weight at 900° C., no lime was liberated. The X-ray pattern of the product indicated a mixture of  $\beta$ - and  $\gamma$ -dicalcium silicate. When this material was then exposed to steam for 11 days at 160° C. and then dried over lime, one mole of water was reabsorbed. The weights of the samples were then the same as the original weights. The X-ray pattern of the rehydrated product, however, showed greater similarity to the fine-grained hydrate first described above than to the original hillebrandite.

## II. EXPERIMENTS WITH TRICALCIUM SILICATE

### *The Products of Hydration*

Experiments on the action of saturated steam on tricalcium silicate over the temperature range 50° to 375° C. were made. One of the most striking characteristics of tricalcium silicate, when brought in contact with water at room temperature, is its violent liberation of lime. When exposed to dry steam this property is modified or may even disappear. At temperatures between 50° and 110° C. some free calcium hydroxide was formed, but the amount of this substance was in general much less than one mole per mole of tricalcium silicate present and did not, therefore, account for a complete decomposition of the tricalcium silicate to hydrated lime and hydrated dicalcium silicate. Further, the amount of water taken up was in excess of the quantity required to hydrate the free lime and the corresponding amount of dicalcium silicate. This indicates that some direct hydration of tricalcium silicate occurred in saturated steam even at temperatures lower than 100° C. The amount of lime liberated decreased rapidly with rising temperature; between 110° and 375° C. very little or no free calcium hydroxide was found in the product, unless other conditions favoring the production of free lime prevailed.

It was found that hydrolysis was favored by the following factors: (1) Low steam temperatures. (2) Moistening of the sample with water or saturated lime-water before the steam treatment. This also accelerated the direct hydration of the silicate. Accidental condensation of water in the crucibles containing the silicate during the treatment, such as might be caused by fluctuations in the temperature of the autoclave, also increased hydrolysis. (3) Slow drying of the treated products, as, for instance, over a saturated solution of potassium chloride (aqueous tension 16.1 mm.) at 21° C., instead of over lime. (4) Use of a large sample; small samples were as a rule found to come through the treatment with less hydrolysis than large samples. This was probably due to the greater chances in the case of the bulkier samples for condensation and retention of liquid when once condensed.

The rate of absorption of water also varied with the temperature in a manner similar to that found with dicalcium silicate. Between 110 and 175° C. approximately 1.5 moles of water per mole of tricalcium silicate was taken up fairly rapidly (2-5 days), while the maximum absorption on further treatment, with subsequent drying over lime, approached two moles. Between 225° and 375° C. about one mole of water was taken up fairly rapidly (less than six hours), further amounts being absorbed very slowly. As with dicalcium silicate, unhydrated centres appeared to persist longer at the higher temperatures.

A large number of samples weighing from 0.1 to 2.0 gm., treated at temperatures between 150° and 350° C. until they had taken up 1.3 to 1.9 moles of water per mole of tricalcium silicate (after drying to constant weight), were found to contain no free lime or only a trace. Rarely were samples thus treated found to contain more than 0.2 moles of calcium hydroxide. This represents one-fifth of the decomposition necessary for the formation of hydrated dicalcium silicate. This indicates that under the conditions of these experiments direct hydration is the predominating reaction, possibly with the formation of  $3\text{CaO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ .

The results of careful microscopic examinations did not give conclusive evidence as to the optical properties of the resulting hydrate of tricalcium silicate. The original grains of tricalcium silicate were broken up by the steam treatment into very finely crystalline material of low birefringence and of mean index 1.59. A number of samples to which lime-water had been added before treatment in the autoclave showed the presence of intergrown sheaves of very small colorless anisotropic prismatic crystals with parallel extinction, and having refractive indices  $\alpha = 1.589 \pm 0.003$ ,  $\gamma = 1.597 \pm 0.003$ . One such sample, which had been moistened with saturated lime-water before treatment and then autoclaved at 185° C. for 120 hr., absorbing 12.5% of water, appeared under the microscope to be composed almost entirely of such intergrown sheaves of crystals. A duplicate sample, except for the treatment with lime-water, absorbed 11.2% of water and had the usual massive crystalline appearance. Both samples gave good X-ray patterns, which were identical. The first sample was found to contain 0.18 moles of free calcium hydroxide per mole of tricalcium silicate, while the second sample contained only a trace, but no lines of calcium hydroxide or of hydrated dicalcium silicate were found in the X-ray diffraction pattern of either sample. While the presence of 0.18 moles of free lime in the samples that contained the prismatic crystals may introduce an uncertainty, yet it seems likely from the X-ray patterns that these crystals and the finely grained hydrated tricalcium silicate usually obtained without any hydrolysis are identical. This X-ray pattern differs from that of the needle-shaped crystals obtained on hydration of dicalcium silicate.

X-ray diffraction patterns were valuable in confirming the analytical and microscopic results. Four patterns made from hydrated samples of tricalcium silicate, containing no free lime or only traces, gave the same pattern, which

differed from any of the patterns so far studied. The readings are given in Table I and Fig. 1-E. The hydration varied from 1.3 to 1.9 moles of water. This suggested again that the amount of water, at least that in excess of one mole, has little effect in determining the crystal structure. Several identical patterns were obtained from hydrated samples containing less than 0.2 moles of free calcium hydroxide, especially samples containing a large quantity of the slender prismatic crystals. On the other hand, hydrated samples of tricalcium silicate that contained more than 0.2 moles of free calcium hydroxide gave patterns containing the strong lines of calcium hydroxide and those of hydrated tricalcium silicate. In the case of one sample that was dried over a saturated solution of potassium chloride and that contained a large quantity of free lime, the pattern showed only the lines of calcium hydroxide and of hydrated dicalcium silicate. No shifting of the lines of the pattern was observed, and thus there was no indication of the formation of solid solution.

The experimental results indicate that tricalcium silicate may hydrate in steam to form a single crystalline hydrated silicate with a limiting composition of  $3\text{CaO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . When conditions favor hydrolysis, decomposition may take place with the liberation of free lime and the formation of crystalline hydrated dicalcium silicate of the composition  $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ , or a mixture of the two hydrated silicates. X-ray diffraction patterns of hydrated tricalcium silicate containing from 1.3 to 1.9 moles of water are virtually identical, indicating that the amount of water over this range is not important in relation to crystal structure. Considering both dicalcium silicate and tricalcium silicate, it would appear that the first portion of water absorbed with the formation of small irregular grains changed the crystalline structure materially from that of the crystals of the anhydrous silicate, but that water then continues to be absorbed without a marked structural change.

#### *Dehydration of Hydrated Tricalcium Silicate*

Carlson (3) has shown that tricalcium silicate, when heated at  $1050^\circ$  to  $1300^\circ$  C., liberates free lime. While the hydrated samples of dicalcium silicate could be dehydrated completely without any liberation of lime, it was found that the hydrated tricalcium silicate was unstable at much lower temperatures than those reported by Carlson for the anhydrous material. A hydrated sample containing 0.2 moles of free lime per mole of tricalcium silicate was found to liberate no further lime on heating in the muffle for four hours at  $500^\circ$  C., while seven hours' heating at  $900^\circ$  C. raised the amount of free lime to one mole, the X-ray pattern showing the lines of  $\beta$ -dicalcium silicate. Other samples of hydrate containing only traces of free lime before ignition were found to liberate a maximum of one mole on prolonged heating at  $900^\circ$  C.

#### *The Hydrolysis of Hydrated Dicalcium and Tricalcium Silicate*

It is of interest to compare the behavior of the hydrated silicates with that of the anhydrous silicate when exposed to a large excess of water. A comparison was made at  $21^\circ$  C. by the method of Thorvaldson and Vigfusson (18).

The hydrolysis curves obtained agreed with those given by Thorvaldson and Vigfusson (18). Thus, when the ratio of water and silicates was adjusted so that the liquid approached saturation with calcium hydroxide at equilibrium, it was found that the silicate in each case had hydrolyzed to  $3\text{CaO} \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$ . The inflexion point in the hydrolysis curve where the solid has a composition of approximately  $\text{CaO} \cdot \text{SiO}_2 \cdot x\text{H}_2\text{O}$  was also observed. The only marked difference was that when the hydrated silicates were used the final hydrolysis equilibrium, more particularly with dicalcium silicate, was attained in a small fraction of the time required with the anhydrous silicate. This suggests that while the first step in the hydrolysis of tricalcium silicate, in the presence of a large excess of water, is the exchange of one molecule of water for one molecule of calcium oxide, a very rapid reaction, the first step in the hydrolysis of anhydrous dicalcium silicate may be a slower hydration of the molecule, the secondary reaction in the two cases being identical, namely, the hydrolysis of hydrated dicalcium silicate.

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## THE ELECTRODE POTENTIAL OF IRON IN RELATION TO HYDROGEN ION CONCENTRATION<sup>1</sup>

By J. W. SHIPLEY<sup>2</sup> AND J. H. SHIPLEY<sup>3</sup>

### Abstract

The electrode potential of iron immersed in phosphate, borate and citrate buffers of varying hydrogen ion concentration was measured, using a normal calomel electrode as the second half of the cell. Breaks in the potential of the iron electrode amounting to as much as 0.7 volts were found to occur at definite pH values for each series of buffers. The electrode exhibited an "initial" and "final" potential depending on the pH of the electrolyte and the time of immersion, the "final" value requiring several days to become established. The "final" break in the electrode potential of 0.74 volts in the pure phosphate buffer occurred between a pH of 3.1 and 4.0, that in the pure borate buffer, of 0.75 volts, occurred between a pH of 4.3 and 4.6, and in the pure citrate buffer, of 0.77 volts, between a pH of 10.1 and 10.9. The effect of chloride ion and de-aeration on the electrode potential was observed. It is suggested that the potential of the iron electrode is determined by the presence or absence of a non electrically conducting film or deposit on the iron, the formation of which is a function of the nature of the electrolyte and its hydrogen ion concentration. De-aeration apparently had no effect on the electrode potential, but the presence of chloride ion affected the establishing of the "final" potential and caused the break in voltage to appear irregularly at a much lower hydrogen ion concentration.

At pH values below that at which the break in potential occurred, corrosion of the iron electrode was marked, and the electrode potential remained high, while, at pH values above the break, corrosion was virtually inhibited or confined to local spots on the electrode, and the electrode potential remained low. The presence of the chloride ion stimulated local corrosion and permitted general corrosion to proceed at a lower hydrogen ion concentration.

### Introduction

Assuming the electrochemical theory for the corrosion of iron, it would be expected that the tendency of iron to dissolve would be a function of the hydrogen ion concentration. The greater the concentration of the hydrogen ions in the solution in contact with the iron, the greater should be the tendency for the iron to dissolve, owing to the formation of ferrous ions. A buffer solution provides a constant concentration of hydrogen ions, and any change in the tendency of the iron to dissolve in such a solution can be attributed, in part at least, to changes in the concentration of the ferrous ions surrounding the iron, or to interference with the passage of ferrous ions into solution, or to interference with the transference of electrons to the hydrogen ions.

The single electrode potential of iron, that is, the driving potential pure iron exhibits in the formation of ferrous ions, normal in respect to the concentration of the latter, is 0.43 to 0.44 volts, hydrogen scale. If an electrolytic cell be assembled in which one element is metallic iron and the other a calomel electrode, both dipping into a buffer solution, then the potential of the iron electrode can be determined by subtracting the constant potential

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of the calomel electrode from the total potential, measured on a potentiometer inserted in the circuit outside the electrolyte. The potential of the iron electrode so determined should give some indication of the tendency of the iron to dissolve, or corrode. Any interference with the production of ferrous ions will lower the positive potential of the iron. Thus the formation on the surface of the iron of a film that is non-porous to the passage of ferrous ions will lower this potential. Such an effect is described by Evans (3, 4) and considered in most treatises on corrosion, such as that by Speller (10). The accumulation of ferrous ions around the iron would also tend to lower the electrode potential in accordance with the Nernst ionic concentration effect. If the electrolyte contains an anion capable of forming a relatively undissociated or insoluble compound with the ferrous ion (or ferric, if aerated), then the concentration of ferrous ions will be fixed in accordance with the ionic equilibria concerned. The formation of films in contact with the iron is possibly the most important consideration in the electrode potential of iron immersed in a buffered electrolyte. McAulay and Bastow (7) found that when a piece of iron is immersed in an air-free electrolyte, it tends to come to a constant potential no matter what the preceding treatment of the iron has been. This would indicate that it is the electrolyte that determines the potential of the iron in contact with it. McAulay and White (8) followed up this work by measuring the electrode potential of iron immersed in solutions of different hydrogen ion concentrations, using potassium chloride and potassium phosphate solutions. This work will be referred to in a later paragraph.

Considering the paucity of information accumulated regarding the effect of hydrogen ion concentration on the electrode potential of iron, it was deemed desirable to carry out an investigation to ascertain what relations might exist between the potentials of iron in buffered solutions of various hydrogen ion concentration and with various anions.

### Experimental

Three series of buffers were chosen, *viz.*, phosphate, borate and citrate. The phosphate buffers covered the range pH 1.8 to 12.1, the borate, 3.0 to 12.1, and the citrate, 2.1 to 12.5. The desired pH was secured by the use of the corresponding acid of the buffer salt and sodium hydroxide. A salt bridge of potassium nitrate in agar-agar protected the buffer solutions from the action of the chloride of the calomel electrode. To one series of each of the three buffer solutions 0.25 gm. of sodium chloride per 100 cc. of solution was added. Another series of the same buffers in which hydrochloric acid was used to adjust the pH, instead of the buffer salt acid, was prepared, and the potentials determined while hydrogen was passing through the electrolyte. A similar set of determinations was made for a duplicate series of buffer solutions, but through which oxygen was passing freely. In the first series sufficient time was allowed for de-aeration by means of the hydrogen gas before the potentials were measured. No significant difference was observed between the potentials of the oxygen and hydrogen series, but the break in



the "final" potential was at a lower hydrogen ion concentration than it was in the pure buffer solutions. This is attributed to the effect of the chloride ion. Apparently the presence of oxygen did not affect to any marked degree the potential existing between the iron and the electrolyte.

The pH values of the buffered electrolytes were determined by means of the hydrogen electrode. The electrodes consisted of a coil of No. 30 iron wire of 99.8% purity, such as is commonly provided for standardizing purposes. The potential existing between the iron wire and the electrolyte was determined on a potentiometer, using the normal calomel electrode as the second element of the cell. Potentials are referred to the hydrogen potential as zero. The results, when oxygen or hydrogen was passing, were obtained without the use of a salt bridge, while, for all other determinations, a salt bridge was used. No correction for liquid junction potentials has been applied.

"Initial" potentials of the untreated electrode were observed as quickly as possible after the electrodes were immersed in the buffer solution.

The "final" potentials were those observed after the electrodes had been immersed for three to seven days in the electrolyte. The potential, after immersion of the electrodes, gradually changes, and the "final" or stable value was attained only after some days. This "final" value was assumed to be reached when three successive readings, each taken after succeeding intervals of one day, did not differ by more than 0.02 volts. In general the greatest change in potential took place during the first few hours after immersion of the electrodes, while the "final" potential was approached more gradually. The nature and pH of the buffer solution, however, also affected the rate of change in potential of the untreated iron electrode.

It should be mentioned also that the results, where hydrogen or oxygen was passing, were obtained with solutions vigorously stirred by the oxygen or hydrogen gas. All other results were obtained with as little disturbance as possible of the electrolyte and immersed iron electrode during and between determinations.

According to Lochte and Paul (6) the over-all potential of the iron electrode against a standard half cell is probably a mean of the potentials of all the local half cells occurring on the electrode. Accordingly, about 18 inches of wire was immersed in the electrolyte. Reproducibility of the average potential of the electrode would be favored by having a large surface exposed to the electrolyte.

Fig. 1 is a graph of the "final" potentials for an iron electrode immersed in pure phosphate, borate and citrate buffered solutions of various pH values, while Fig. 2 is a similar graph for the same solutions but to which a small amount of sodium chloride had been added. It will be observed from Fig. 1 that the breaks in potential are quite definitely a function of the hydrogen ion concentration, and occur at a different pH for each of the three buffer solutions. The effect of the chloride ion on the potential of the iron is well illustrated in Fig. 2, where the drift of the potential with change in pH is quite irregular and the position of the breaks is far from definite. Never-

theless in each buffer solution there is a downward drift of potential with decreasing hydrogen ion concentration, but the breaks are ill-defined and occur at a distinctly lower hydrogen ion concentration than in the case of the pure buffer solutions.

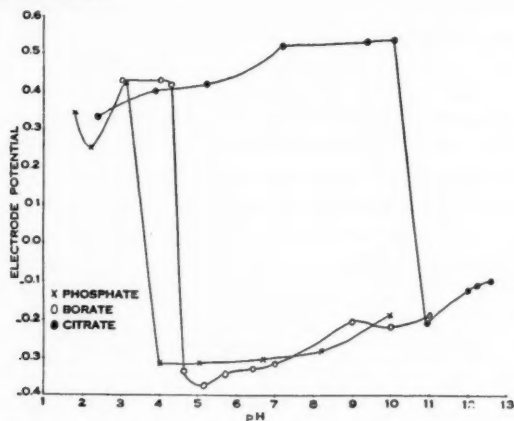


FIG. 1. Potential of iron electrode in phosphate, borate and citrate buffered solutions, referred to hydrogen as zero.

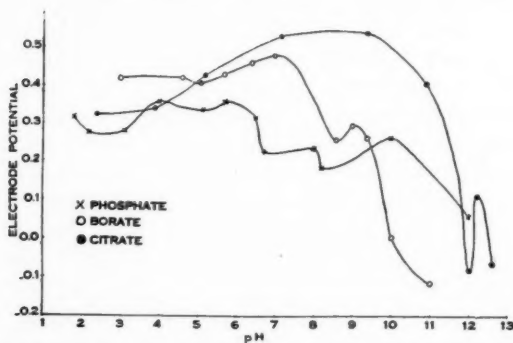


FIG. 2. Potential of iron electrode in phosphate, borate and citrate buffered solutions to which sodium chloride was added, referred to hydrogen as zero.

A drop of more than 0.7 volts occurred in the potential of the electrode immersed in the pure phosphate buffered solution between a pH of 3.1 and 4.0. In the pure borate buffered solution there is a similar drop in potential between a pH of 4.3 and 4.6, and in the pure citrate buffered solution the drop lies between a pH of 10.1 and 10.9.

#### Passivity

Wherever the "initial" potential was low, it is to be assumed that the electrode was in a passive condition when immersed in the electrolyte. On the other hand, if the "initial" potential was of the order of 0.4 volts, it is to

be assumed that the electrolyte removed the passivity of the iron wire before measurement could be made. Not only were such differences observed but also cases in which long immersion in the electrolyte changed the potential of the iron either from an initial state of passivity to an active state or *vice versa*. For example, in the pure phosphate buffers the "initial" potential up to a pH of 5.1 registered a voltage in the neighborhood of  $+0.4$ , but on long immersion at pH values of 4.0 and 5.1 the potential dropped to  $-0.3$ , a drop of 0.7 volts. This would indicate that the original passive state of the iron was removed by immersion in the electrolyte, but that on longer immersion the passivity was restored, possibly by the formation on the surface of the iron of a protective coating of a corrosion product through which the ferrous ions were unable to pass into solution. The opposite effect was noted with the phosphate buffer containing sodium chloride in solution. At pH values above 6.5 the "initial" potential was about  $+0.07$  volts, but on long immersion the potential rose to about  $+0.25$  until a pH of about 12.0 was reached. Apparently the effect of the sodium chloride is to remove the passivity; that is, to destroy or render electrically conducting the passivating coating or film.

In order to test the assumption that the iron wire was probably in a passive condition before it was immersed in the electrolyte, a direct current of 4 volts was passed through the electrolyte, with the iron wire already in the "final" condition as the cathode, and a platinum wire as anode. Within a time interval of one second after breaking the current the potential of the iron electrode was determined, and in every solution, phosphate, borate and citrate, over the whole pH range involved, the potential of the iron electrode was found to be about 0.8 volts. After a few hours or longer the potential fell to approximately that exhibited by the electrode when in its previous "final" condition in the electrolyte. This would indicate that it is the effect of the electrolyte on the iron which determines its "final" potential. Cleaning the surface of the electrode with emery paper after it had reached the "final" potential and immediately re-immersing it in the electrolyte, gave a voltage reading of approximately 0.3 volts higher than the "final" reading. This potential of the immersed electrode gradually fell to the original "final" reading.

Treatment of the iron wire with concentrated hot solutions of hydrochloric acid, nitric acid and potassium dichromate did not affect the "final" potential when the wire was immersed in the buffered solutions. In each case the wire reached the same potential as that of an untreated iron electrode.

A few determinations were made on the effect of dilution of the buffer solution on the electrode potential of the iron. All three series of buffers were used, but any departure from the potential effects already observed was noted only in the case of high dilution and the higher pH values. In high dilutions there was a tendency for the potential to approach the value shown for iron in pure water.

### *Corrosion*

Although the experiments were not primarily designed to provide a method for ascertaining the extent of the corrosion of the iron electrodes, yet certain observations linked the progress of corrosion with the change in pH of the electrolyte and the potential of the iron. The accumulation of ferrous phosphate in the Pyrex flasks gave a qualitative measure of the extent of the corrosion in this series of buffers. At all pH values below 4.0 the accumulation of ferrous phosphate was quite marked, and increased progressively with the decrease of the pH. In the flask containing pure phosphate buffer at a pH of 1.8, the iron wire was disintegrated into short pieces. At pH values between 4.0 and 6.7 there was a little of the ferrous phosphate to be observed, but it became progressively less in each flask as the pH rose. At a pH of 6.7 there was no ferrous phosphate visible, but the iron wire in one sample was covered with a grayish-black coating, while in another of the same pH the wire remained bright over a period of three months. At all pH values above 6.7 the iron wire remained as bright as when introduced into the electrolyte. Thus at pH values below 4.0 the corrosion was progressively greater with time, while at pH values above this the corrosion was inappreciable. The voltage break found in the "final" readings occurs in the neighborhood of this marked change in the extent of the corrosion.

The amount of white precipitate of ferrous phosphate in phosphate buffers containing sodium chloride became definitely less as the pH rose, until a pH of 6.7 was reached, when sections of the wire were observed to remain quite bright. Nevertheless local corrosion could be observed on the wire at all the higher pH values. Apparently local corrosive action is stimulated in phosphate buffers by the presence of the chloride ion.

In the series of borate buffers a definite "break" in voltage occurs between pH 4.3 and pH 4.6, the fall in voltage being common to both the "initial" and the "final" potentials. The relation of this break to the progress of the corrosion was plainly shown in the accumulation in the electrolyte of corrosion products of the iron. In the electrolyte of pH 4.3 and lower there was an accumulation of reddish brown products of corrosion, and the iron wire was covered with a brown coating, while, at a pH of 4.6 and higher, the wire remained bright and no precipitate was in evidence.

In the borate buffers containing sodium chloride, reddish corrosion products and a general coating over the wire were observed up to a pH of 7.0. At a pH of 8.6 and above, only local corrosion spots were in evidence, while sections of the wire remained bright. Apparently general corrosion of the electrode ceases at a pH of about 7. Again it will be noted that evidence of a "break" in the electrode potential occurs in the "final" readings at about this pH. The stimulation of local spots of corrosion by the presence of the chloride ion was very marked in the borate buffers.

The citrate series of buffers were altogether different in respect to the accumulation of products of corrosion. None were in evidence below a pH of 3.9, the electrolyte remaining colorless, and no evidence of iron in solution

could be obtained by treating a sample with hydrochloric acid and testing with potassium thiocyanate. However the iron wire was not bright. At a pH of 3.9 the electrolyte was slightly green, and on treatment with hydrochloric acid and potassium thiocyanate showed the presence of a little iron. At a pH of 5.2 the greenish color was very marked and increased in intensity up to a pH of 7.2. At pH values above 10.1, where the break occurs, there was no greenish color in the electrolyte and the wire remained bright.

Citrate buffers containing sodium chloride exhibited no greenish color below a pH of 3.9. At a pH of 3.9 the electrolyte was greenish and contained considerable amounts of iron in solution. The amount of iron increased up to a pH of 7.2, was less at a pH of 9.4 and there was none at a pH of 12. There was a little local corrosion in a solution of pH 12, but none above this pH value, the iron remaining bright. It is to be observed that the break in the "final" potential occurs between the pH values 10.9 and 12.0, and amounts to 0.48 volts.

The most remarkable fact in the corrosion of iron in citrate buffers is that it does not proceed at pH values below 3.9 or above a pH of 12, but does proceed in an intermediate range of pH values, reaching a maximum in the neighborhood of pH 7.2. A similar observation was made by Bryan (1) in a study of the rate of oxidation of ferrous citrate solutions.

These observations on the corrosion of iron in buffered solutions definitely showed that a close relation exists between the rate of corrosion and the potential of the iron in the electrolyte. At pH values lower than those at which the "break" in electrode voltage was observed, continuous general corrosion of the wire occurred, while at pH values above this, general corrosion was absent and corrosion in local spots accelerated by the presence of chloride ions alone took place. The rate of corrosion increased with decreasing pH, except in the case of the citrate buffer series, where both general and local corrosion did not occur at a pH below 3.9.

### Discussion

McAulay and Bastow (7) observed that when iron was immersed in 2*N* potassium sulphate solution, the potential of the iron reached a definite value of about 0.4 volts, no matter what the previous treatment of the specimen of iron had been and largely independent of the composition of the iron. This condition of constant potential they describe as a "standard state". This corresponds to the potentials at pH values higher than that at which the break in the "final" potentials described in this paper occurred, and as suggested by them was found to be a function of the pH of the solution. The difference in potential of the iron before and after the break is about 0.7 volts, the iron becoming enobled to that extent. McAulay and White (8), using a phosphate series of buffers, found the break in potential of the iron to occur between a pH of 7.5 and pH 8.5, while in our series it occurs between the pH values 3.1 and 4.0 when the chloride ion was not present. It will be noted also that when sodium chloride was present in the phosphate buffers the



break in the potential did not occur until a pH of 8.0 was reached, and that the difference of potential above and below the break was only about 0.18 volts, instead of 0.7 volts as in the case of the pure phosphate buffers.

The break in the case of the pure borate series of buffers occurs at a pH of about 4.3, and, as with the phosphate series, the presence of chloride ion causes the break to occur at higher pH values, probably in the neighborhood of pH 9.

In the pure citrate buffers the "final" break in potential is at a pH of 10.1, and in the neighborhood of 11.0 when chloride ion is present. As with the phosphate and borate buffers, the magnitude of the drop in potential at the "break" is much less than when chloride ion is absent.

Chittum (2) determined the electrode potential of iron immersed in a series of phosphate buffered solutions, but as his readings of potential were taken shortly after immersion of the iron no comparison can well be made with those given in this paper. It required several days for the electrode to come to equilibrium with the electrolyte, particularly at pH values in the neighborhood at which the break in the potential occurred. Moreover the disturbing effect of the chloride ion present in Chittum's solutions might be expected to give irregularities such as are observed in Fig. 2. in this paper.

More regularity was observed in the potential drift in the writers' experiments when oxygen and hydrogen were bubbling through the solution. Stirring was not resorted to in the other experimental work, as it was considered undesirable to disturb film formation, and, moreover, local corrosion spots could not then have been so readily detected. More regularity in potential readings would be expected had the iron electrode been rotating.

It is a remarkable fact that electrolytes of the same composition and pH gave the same electrode potentials when hydrogen was bubbling through as they did when oxygen replaced the hydrogen. This held true for all three series of buffers and for both the "initial" potential and the "final".

The nature of the buffer solution and its pH are the significant factors so far as the breaks are concerned. This does not agree with the conclusions of McAulay and White (8), who consider that the presence or absence of oxygen affects the formation of films on the electrode. According to Forrest, Roetheli and Brown (5), gelatinous ferric hydroxide and magnetic oxide of iron are film forming compounds in oxygenated distilled water, the former being particularly resistant to the diffusion of ions. In the citrate and phosphate series of buffers, ferric hydroxide was not observed, but nevertheless in these series of buffer solutions, breaks in the potential of the iron electrode occurred similar to those observed in the borate series in which ferric hydroxide was visibly apparent.

The breaks in the potential of the electrode are possibly associated with the fact that films on the iron affect the passage of ferrous ions into solution. The "initial" voltage of the iron in the pure phosphate buffers was about +0.40 volts, until a pH of 5.1 was reached, when it dropped to -0.02. It is assumed that at pH values below 5.1 the electrolyte removed the passi-



vating film from the surface of the electrode immediately after its immersion, but at pH values above 5.1 this removal did not take place. However, at pH values between 3.1 and 5.1 long immersion gave a "final" potential of  $-0.31$ , a drop in voltage of  $0.7$  occurring without any change in the pH of the electrolyte. This drop in potential may have been due to the formation of a secondary non electrically conducting film formed after the electrolyte had removed the original passivating film.

The relatively long time required for this film to become non electrically conducting could be explained by the slowness with which ferrous ions were going into solution, and the chance deposition of the compound where pores existed in the protective film or where it was particularly thin. This gradual building up of the protective film with increasing electrical resistance would also account for the gradual drop in potential observed between the "initial" and "final" potentials, as in the case of the pure phosphate buffers between a pH of 3.1 and pH 5.1. Where the "initial" and "final" potentials are both low, the original passivating film on the electrode is probably not removed by the electrolyte, and if the "final" potential be lower than the "initial" low potential, the second film may be considered as superimposed on the first. In every case in which chloride ion was absent, the "final" potential at pH values above that at which the break occurs was always lower than the "initial" potential.

Between pH values of 3.9 and 10.9, the "initial" low potential of about  $-0.1$  volts in pure citrate buffers rises after long immersion of the iron in the electrolyte to a final potential of  $+0.5$  or higher. This would indicate that immersion in the electrolyte brought about the removal of the passivating film originally on the iron.

At and above a pH of 10.9 the citrate electrolyte does not affect this film and the potential remains low. No insoluble compound appeared to be formed in the citrate buffers, and none of the potentials were found to be lower than that of the "initial" low. Apparently no secondary film is formed. This is also evidenced by the high potentials of the "final" reading between pH values of 3.9 and 10.9.

The effect of the chloride ion on the film may be to render it electrically conducting to the ferrous ion, and in all buffers containing chloride ion the "final" potentials are irregularly higher than the corresponding potentials in the same buffer having no chloride ion but of the same pH. Another effect of the chloride ion is to stimulate local corrosion cells on the electrode. These cells in themselves would be a disturbing factor, not only on the continuity of the protective film but also upon the composite electrical potential of the iron electrode.

The earlier work of one of the authors (9) showed that there is a relation between the rate of corrosion of iron and the solubility of ferrous hydroxide as affected by hydrogen ion concentration. A drop in potential as great as  $0.7$  volts, as found in the present experimental work and observed to be a function of the hydrogen ion concentration of the electrolyte, cannot be

explained satisfactorily on the basis of the Nernst ionic concentration effect or of hydrogen overvoltage. Apparently the controlling factor in establishing the electrode potential of the iron is the formation of ferrous ions from the electrode and the freedom of passage of these ions into solution. The nature of the surface of contact of the iron with the electrolyte is the all-important factor in determining the formation of ferrous ions and, consequently, the corrosion of the iron in the absence of an external e.m.f. It appears necessary to assume the presence of a non electrically conducting film or coating on the iron in order to explain the inhibiting effects of the electrolyte on the free passage of ferrous ions into solution. Ionic equilibria established in the electrolyte can hardly afford an explanation of the phenomena observed, unless related to the establishing of a non electrically conducting film. It is highly important in considering the phenomena relative to the corrosion of metals that we learn more about what happens at the surface where ion formation is occurring.

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## THE PROPERTIES OF SALT-CLAY ROAD-SURFACING MIXTURES<sup>1</sup>

By A. F. GILL<sup>2</sup>

### Abstract

This paper describes experiments designed to throw light on the mechanism underlying the beneficial effect that had been observed in field trials of salt treatment of clay road surfaces. Data are presented which show that no chemical reactions are involved, and that physical-chemical effects are of negligible importance. The results indicate that the main effect of salt additions to the clay is a greatly decreased rate of drying, together with, under ideal conditions, complete elimination of drying shrinkage.

### Introduction

The experimental results which are presented herein were obtained in an investigation made early in the year 1933. The object of the work was to secure an explanation of the benefits which had been claimed for the use of salt-clay mixtures in certain experimental highways constructed in the province of Nova Scotia. The increasing interest which has since been shown in this method of construction both in Canada and the United States has prompted the publication of the results obtained in the original experiments.

When the problem was first undertaken consideration was given to various suggestions which had been put forward to account for the observed effect of salt in admixture with clay:

- (1) That chemical reaction occurs.
- (2) That coagulation of colloidal clays is the principal factor.
- (3) That the action of the salt is primarily physical.

A number of those connected with the early field experiments were of the opinion that chemical reaction was involved. While the author recognized that a type of zeolite transformation might occur when a comparatively large excess of sodium chloride came into contact with certain double silicates which might be present as impurities in clays, there appeared to be no reason to believe that the aluminium silicate portion of a clay could undergo any significant reaction with sodium chloride.

The part played by sodium chloride in coagulating the more colloidal clays is well recognized. Coagulation would presumably decrease the deformation of the clay under load and might also be of advantage in lowering the normal water absorption.

Salt might have a physical effect upon clay in several ways. It would be expected to decrease the vapor pressure of mechanically held water and thus prolong its period of drying. Possibly, also, the growth of sodium chloride crystals as the water evaporated would have the effect of stiffening and reinforcing the clay mass.

<sup>1</sup> Manuscript received August 29, 1935.

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada.

<sup>2</sup> Chemist, National Research Laboratories, Ottawa.

### Experimental

The laboratory experiments were carried on largely with a sample of a clay that had been used in the highway trials. This was known as Elmsdale clay. Analysis:  $\text{SiO}_2$ , 61.4;  $\text{Fe}_2\text{O}_3$ , 5.8;  $\text{Al}_2\text{O}_3$ , 23.3;  $\text{CaO}$ , 0.6;  $\text{MgO}$ , 1.5;  $\text{TiO}_2$ , 0.3; water at  $105^\circ \text{C}$ ., 2.6; loss, 7.5%. As received in the laboratory, it was a fairly soft material of reddish color. It was passed through a disc pulverizer, set at about 60 mesh, in order to prevent the formation of lumps on tempering with water.

"Malagash" salt, also used in the road tests, was employed in the investigation. Analysis of a sample received: Moisture, 0.27; insoluble, 1.37; sol. Fe,  $< 0.00005$ ; sol. Ca, 0.083; sol. Mg, 0.021; sol.  $\text{SO}_4$ , 0.146; sol.  $\text{CO}_3$ , 0.02; NaCl, 98.5%.

A sample of silica was also employed for comparison with the clay (see Fig. 5). The chemical analysis of this material was as follows:  $\text{SiO}_2$ , 95.3;  $\text{Al}_2\text{O}_3$ , 2.3;  $\text{Fe}_2\text{O}_3$ , 3.0;  $\text{CaO}$  and  $\text{MgO}$ , 0.15, gain on ignition, 0.4%. This material was ground in bulk in a pebble mill until it passed 200 mesh. The water absorption of the resultant product was approximately the same as that of the clay, although the characteristic plasticity of the clay was, of course, lacking. Other materials used in the tests were of reagent grade.

Preliminary tests of the effect of the commercial salt and of c.p. sodium chloride on water suspensions of the clay showed in both cases a noteworthy coagulating action in dilute solution. Ferric chloride, which is recognized as a more active coagulant, was considerably more effective. Actually, however, this clay was comparatively high in non-colloidal material, and the proportion of it that was sufficiently dispersed to remain in suspension for more than a few minutes was small. It did not seem likely, therefore, that even pronounced coagulation of the finest particles would have any very marked effect on the load-bearing capacity or other mechanical properties of the clay in the absence of any other factor. This opinion was borne out by the results of qualitative trials of the comparative resistance to deformation of freshly tempered clay specimens in the pure state and in admixture with different quantities of salt.

In addition it was recognized that in a road surface under normal moisture conditions there would be a tendency for the salt to be present as a saturated solution. This concentration of sodium chloride is of a vastly greater order of magnitude than that required for coagulation or other colloid phenomena.

It was observed, however, that when amounts of salt of about 10 and 20% were added to this clay and the mixture tempered with water, moisture retention at normal room humidities was markedly increased. As this seemed to be the most hopeful avenue of investigation, quantitative determinations were made of the comparative rate of loss of moisture from clay specimens to which had been added respectively ferric chloride, calcium chloride and salt. These results are given in Figs. 1, 2 and 3.

In order that these tests might have a common basis for comparison, each mixture containing 200 gm. of dry clay, tempered with 55 cc. of water to a

plastic consistency, and with the required amount of reagent added, was placed in a 5 in. watch glass and finished with a smooth surface flush with the edges. As the quantity of water was insufficient to dissolve the larger amounts of salt, the latter was added in a finely pulverized form in order to

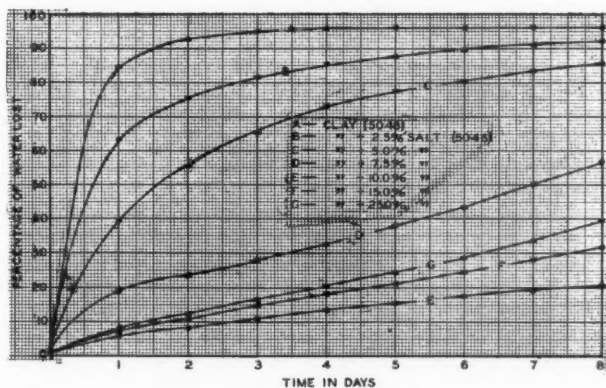


FIG. 1. Comparative rate of loss of moisture from tempered samples at 40° C.

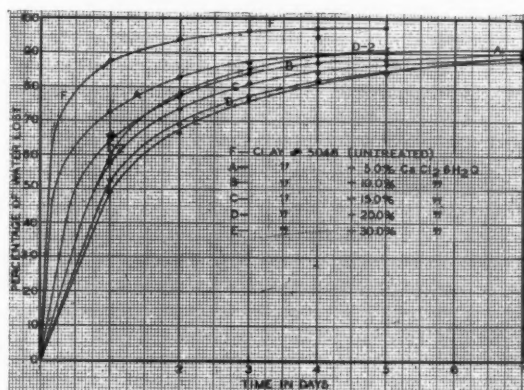


FIG. 2. Comparative rate of loss of moisture from tempered samples at 40° C.

give as uniform distribution as possible. This method minimized the error due to differences in bulk brought about by salt additions, and ensured approximately the same unit surface area per weight of clay or water in each case. The drying tests were carried out at 40° C. in laboratory ovens, in which air of about 35% relative humidity at room temperature was free to circulate. This indicates a relative humidity within the ovens of somewhat less than 15%.

Figs. 1 and 3 show the remarkable increase in moisture retention brought about by the salt additions, compared with the negligible effect of ferric

chloride. The fact that ferric chloride was found to be more effective than the salt as a coagulant of this clay is evidence that no significant relation exists between the two effects.

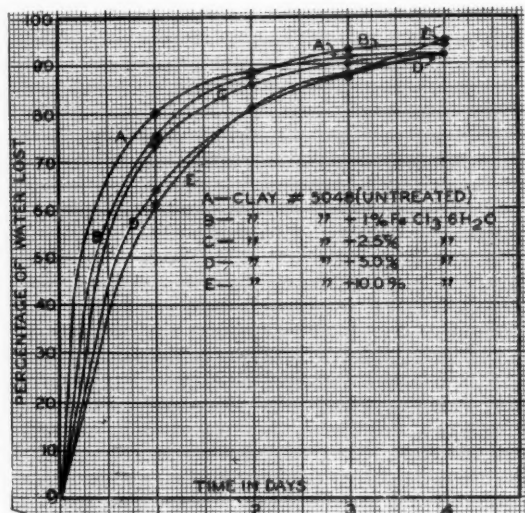


FIG. 3. Comparative rate of loss of moisture from tempered samples at 40° C.

Comparison of the action of sodium chloride and calcium chloride, as indicated in Figs. 1 and 2, respectively, shows that at the temperatures used sodium chloride has an effect markedly greater than that of calcium chloride. The results indicate that, when subjected to the action of a hot summer's sun, a road surface containing sodium chloride would hold its moisture considerably better than one with admixed calcium chloride. However, this would not necessarily be the case at high relative humidity.

The fact that a proportion of 10 to 15% of salt is the most effective in retarding evaporation from the clay is of considerable interest. The evaporation of water and the growth of salt crystals would both tend to increase the porosity of the clay mass. The voids might serve as thermal insulation and, in addition, tend to maintain a comparatively high partial pressure of water within them. This explanation is supported by the fact that, in the tests whose results are shown in Figs. 1, 2, and 3, all the specimens in which ferric chloride and calcium chloride were incorporated cracked through shrinkage in the course of a few days, whereas those containing salt in proportions of 10 and 15% showed no shrinkage cracking. Actually some expansion was observed. Microscopic examination of the surfaces under low-power magnification showed clusters of relatively large sodium chloride cubes. The fact that, with salt contents higher than 15%, cracking occurred and the rate of moisture loss was greater, might be explained on the basis that as the pro-



portion of sodium chloride increased above the optimum its beneficial effect was nullified by the fact that the larger crystals could give decreased surface areas and voids per unit volume of clay.

Fig. 4 indicates that the salt enhances the rate of moisture absorption by the clay when the humidity is high. The fact that there is also evidence of an optimum percentage of salt in respect of water absorption supports the

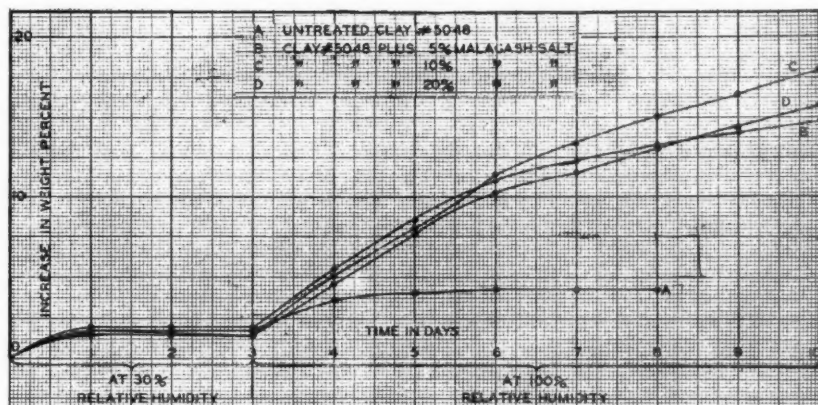


FIG. 4. Comparative rate of gain in moisture of oven dried samples.

belief that capillarity and porosity are important factors. It is noteworthy, however, that the salt has no significant effect on the normal "regain" of this clay at 30% relative humidity.

In Fig. 5 are shown drying curves for salt-silica mixtures. The specimens for these tests were made up in the same way as the clay specimens, the silica being prepared as described above and the proportion of tempering water being the same. These curves show that the effect of the salt on the clay is

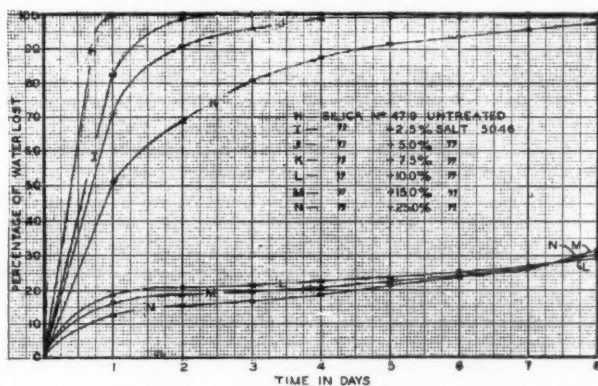


FIG. 5. Comparative rate of loss of moisture from tempered samples at 40° C.

primarily a physical one, for there could be no conceivable reaction at ordinary temperatures between sodium chloride and silica. Figs. 1 and 5 are in qualitative agreement in indicating that 10 to 15% of salt has a maximum effect. A salt-silica mixture would, however, be of little practical use in road construction owing to its lack of cohesion and bonding power.

On the basis of these tests, it was recommended that the salt-clay treatment be given thorough practical trials. The value of the salt will be appreciated when it is considered that so-called "soil concrete" when properly compounded consists of a graded coarse to fine aggregate containing gravel or stone, plus a fine material, such as sand, so proportioned as to give maximum density when bonded with clay. Theoretically, the proportion of clay could be so small that it would serve merely as an adhesive, and its shrinkage and brittleness would be of minor importance. Actually, however, the need of obtaining a material of sufficient plasticity that it will compress readily, requires the use of considerably more clay than would otherwise be necessary. When salt is not added, this clay dries fast, shrinks, and becomes brittle. The shrinkage causes it to pull away from coarse aggregates and allows them to be dislodged under power traffic. This tendency is accentuated by the brittleness. When salt is added, the clay remains putty-like for a longer period, shrinkage is minimized and, under ideal conditions, even eliminated. This results in a comparatively tough, resilient road surface.

#### Acknowledgments

The author wishes to acknowledge the co-operation of Mr. A. R. Chambers, of Prof. R. deL. French of McGill University, who has done considerable work in this field, and of Mr. T. H. Way, research assistant, who made a number of the determinations.

### NOTE ON ISOTOPES IN SNOW AND RAIN WATER

A sample of snow water from the first part of an April snow flurry was investigated by the balanced-float method (2) with accurate temperature control. Both snow water and control water were treated according to the procedure of Washburn and Smith (3). The writers' Experiments 1, 2 and 3 showed a decrease in density of the snow water of  $3.9\gamma$ ,  $3.9\gamma$  and  $4.6\gamma$ ; and Experiments 4 and 5, done 10 weeks later,  $3.9\gamma$ , and  $3.9\gamma$  (No. 3 is probably in error).

It appears that in the constantly varying temperatures in April there is an appreciable fractionation of water into its isotopic forms.

Since the completion of this work a paper by Harada and Titani (1) has come to our attention. In this the changes in densities of winter snow water are given as  $-1.5\gamma$ ,  $-0.5\gamma$ ,  $-3.3\gamma$ ,  $-1.9\gamma$ . One might expect perhaps that a greater fractionation would be obtained in the Spring than in mid-winter. Harada and Titani (1) report an increase in density for the first portion of a rainfall of  $+1.2$  and  $1.6\gamma$ . We have found that the first portion of a shower collected on October 3 gave a difference in density of  $-1.2 (\pm 0.2)\gamma$ .

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